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# Investigations on the effect of preparation conditions on $AgNbO_3$ ceramics

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ABSTRACT

$AgNbO_3$ ceramic was found to be one of the candidate materials for lead-free piezoelectric materials. The processing and sintering procedures have detrimental effect on the characteristics of the ceramics. Ceramic pellets of silver niobate, $AgNbO_3$ were prepared by solid-state reaction technique. To investigate the effect on the ceramic characteristics, two different sintering procedures were adopted. The crystallinity and surface morphology of the prepared samples were investigated by XRD and SEM techniques. The samples prepared by both the methods show orthorhombic structure at room temperature. Comparisons of lattice parameters, crystallite and grain sizes of $AgNbO_3$ are reported. Frequency variations of dielectric constant ($K$), tangent loss ($\tan\delta$) and electrical conductivity ($\sigma$) were measured at room temperature in the frequency range 1 Hz to 10 MHz.



## 1. Introduction

The piezoelectric ceramics have been used for various electronic products. The most used piezoelectric ceramics are lead compounds e.g. PZT due to their higher electromechanical coupling coefficient ($k$) and higher piezoelectric constant ($d$). However, these heavy metals are considered as one of the origins of environmental pollutions. Therefore, the lead-free piezoelectric materials with high piezoelectric performance are of current interest to materials researchers. The ferroelectric $AgNbO_3$ ceramic was found to be one of the candidate materials for lead-free piezoelectric materials. Preparation of such lead-free ceramics is of great interest today. The variables such as purity, stoichiometry and particle size, aggregation state, processing and sintering procedures have a marked effect on their characteristics. The crystalline, physical and electromechanical properties of ferroelectric material greatly depend on the preparation method. 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. In addition, in ceramics, there are possibilities of forming new phases, polymorphic transformations, and decomposition of crystalline compounds. Silver niobate ($AgNbO_3$) is a member of the perovskite niobate. Due to technological importance and tremendous technological potential silver niobate [1,2] and its mixed systems: silver tantalum niobate [3–5], silver sodium niobate [6–8], silver potassium niobate [7,9] and silver lithium niobate [10–14] have been studied by several researchers. The development and improvement of electronic systems must be preceded by the designing of new miniaturized and suitable components. Although existing commercial components meet the engineering criteria, other new systems can be developed or existing ones can be perfected by introducing new components with improved characteristics. This development encourages the investigations of electronic materials, in particular the development of dielectric materials with specific dielectric properties that are required for specific applications. The processing and sintering procedures plays an important role in the characteristics of ceramics with and without additives. Valant et al. [3] studied the micro-structural and dielectric properties of $Ag(Nb_{1-x}Ta_x)O_3$ compositions made by three different processing ways: milling for 30 min at 150 rpm in a $ZrO_2$ mill; hand-grinding; and granulating to obtain three different particle size distributions.

In the present study, ceramic pellets of silver niobate, $AgNbO_3$ were prepared by two different sintering methods. The values of

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**Table 1**
Lattice constants and average crystallite/grain sizes for $AgNbO_3$ prepared by two different methods at room temperature.

| S. no. | Compositions | Lattice parameters | | | Crystallite size (XRD) (μm) | Grain sizes (SEM) (μm) |
|---|---|---|---|---|---|---|
| | | *a* (Å) | *b* (Å) | *c* (Å) | | |
| 1 | $AgNbO_3$ (Ist method) | 5.5972 | 5.5423 | 3.9100 | 0.0212 | 5.127 |
| 2 | $AgNbO_3$ (Ist method) | 5.6035 | 5.5473 | 3.9109 | 0.0223 | 7.472 |

lattice parameters, crystallite and grain sizes of $AgNbO_3$ were investigated. Frequency variations of dielectric constant ($K$), tangent loss ($\tan\delta$) and electrical conductivity ($\sigma$) were also measured and compared.

## 2. Experimental details

The ceramic samples of silver niobate ($AgNbO_3$) were prepared by solid-state reaction and sintering method. The starting materials used for preparing $AgNbO_3$ were silver oxide ($Ag_2O$), purity 99% [*Qualigens fine chemicals*], and niobium pentaoxide ($Nb_2O_5$), purity 99.9% [*Loba Chemie*]. The starting materials were initially dried at 200 °C for 2 h to remove the absorbed moisture and then quantities of the reagent were weighed in stoichiometric proportion. After weighing and mixing the starting chemicals $Ag_2O$ and $Nb_2O_5$, the samples of silver niobate ($AgNbO_3$) were prepared by the following two sintering methods.

### 2.1. Ist method (calcination method)

The ground and mixed powder was again wet-mixed using methyl alcohol in a pestle and mortar for 2 h. The grounded powder was calcined at 850 °C for 3 h for solid-state reaction. The powder was grounded and pellets were made using a pelletizer of 11 mm diameter applying pressure of 3 tons. The prepared pellets were placed on a silica crucible and sintered in air atmosphere at 1050 °C for 12 h. These light yellow color pallets were used for the experiments.

### 2.2. IInd method (three-step sintering method)

In this method the mixed fine powder was wet-mixed using methyl alcohol in a pestle and mortar for 2 h. The powder was grounded and pellets were made as above in the Ist method. These pellets were sintered for 3 h at 850 °C in a silica crucible. The sintered pellets were crushed, milled and mixed for 2 h and again pressed into pellets. The pressed pellets were sintered at 1040 °C for 2 h. Again, the above sintered pellets were crushed, milled, and mixed for 1 h and pressed into pellets and finally sintered at 1100 °C for 3 h. A light yellow color and good quality ceramics have been obtained.

The sintered pellets obtained by both the methods were used for SEM characterization and dielectric measurements. The prepared ceramic samples were characterized for phase and crystallinity by powder X-ray diffraction technique using *D-8 ADVANCE* X-ray diffractometer (Bruker). Surface topography of the prepared samples was studied by scanning electron microscopy (SEM) using LEO-440 scanning electron microscope. Crystallite and grain sizes were determined using XRD and SEM data. Capacitance, resistance, and dissipation factor (tangent loss) measurements were carried out in metal–insulator–metal (MIM) configuration using Solarton 1260 impedance gain phase analyzer. The variations in dielectric constant ($K$), tangent loss ($\tan\delta$) and electrical conductivity ($\sigma$) were measured for $AgNbO_3$ prepared by both the methods in the different frequency ranges.

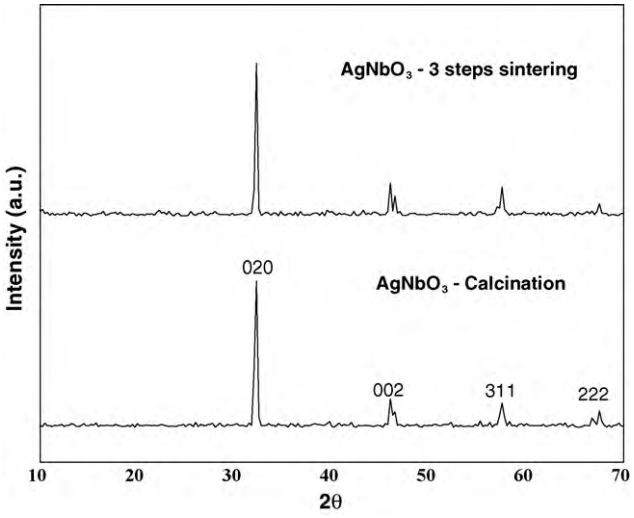


**Fig. 1.** Powder XRD pattern for $AgNbO_3$ ceramics prepared by both the methods.

## 3. Results and discussion

The light yellow color pallets of $AgNbO_3$ were obtained by two different sintering methods. The prepared ceramic samples 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 $2\theta$ ranges of 10–70° with a scan step of 0.02°. Fig. 1 shows the X-ray diffraction patterns for $AgNbO_3$ ceramic prepared by two different methods. From the observed diffraction patterns the lattice spacing was determined which was used to determining the unit-cell 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 pattern of silver niobate prepared by both the methods are same. The lattice constants of $AgNbO_3$ prepared by both methods are shown in Table 1. The calculated lattice parameters shows that at room temperature $AgNbO_3$ system is in orthorhombic phase. The lattice parameters for $AgNbO_3$ are nearly same but the peak intensity of reflected X-ray beam for the sample made by second method i.e. three-step sintering is high. It is understood that the crystallite sizes for the samples made by IInd method

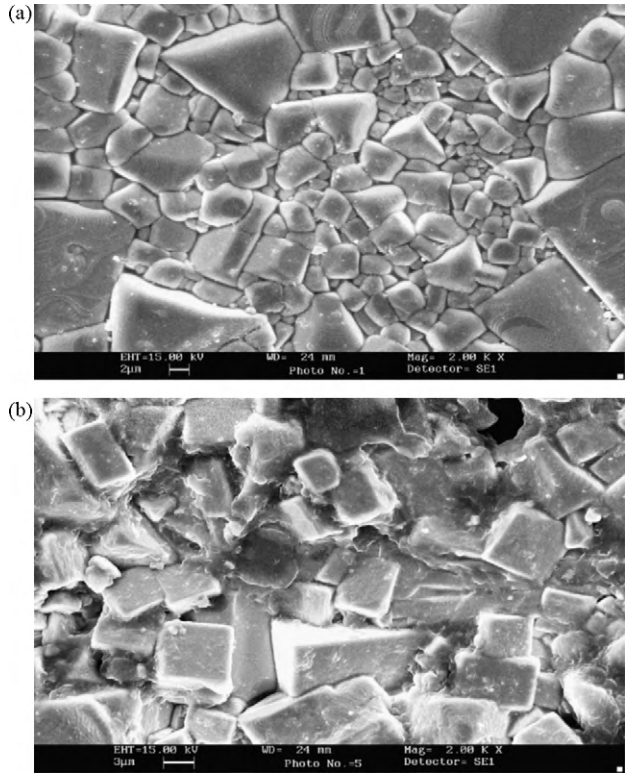


**Fig. 2.** Scanning electron micrographs for $AgNbO_3$ prepared by Ist method (a) and IInd method (b).

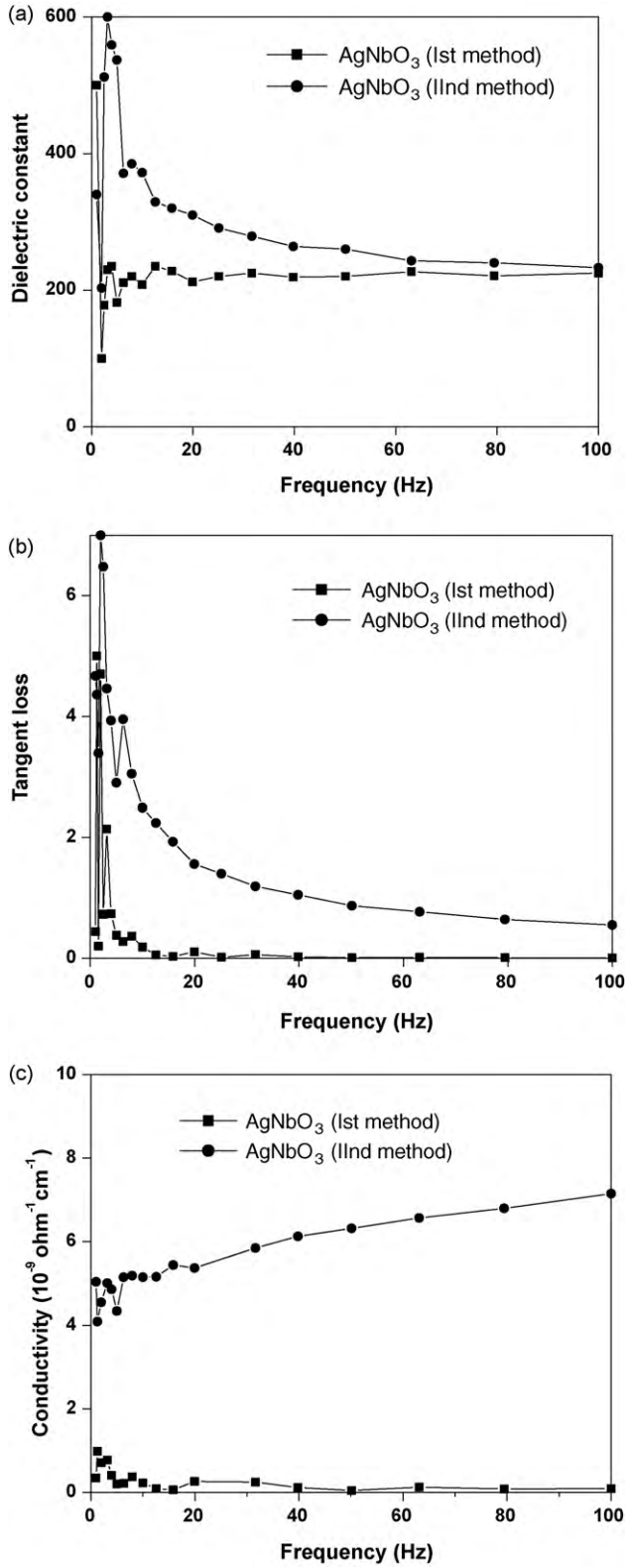


**Fig. 3.** Variation of dielectric constant, loss tangent (tan $\delta$) and conductivity ($\sigma$) with frequency in the frequency range 1 Hz to 100 Hz.

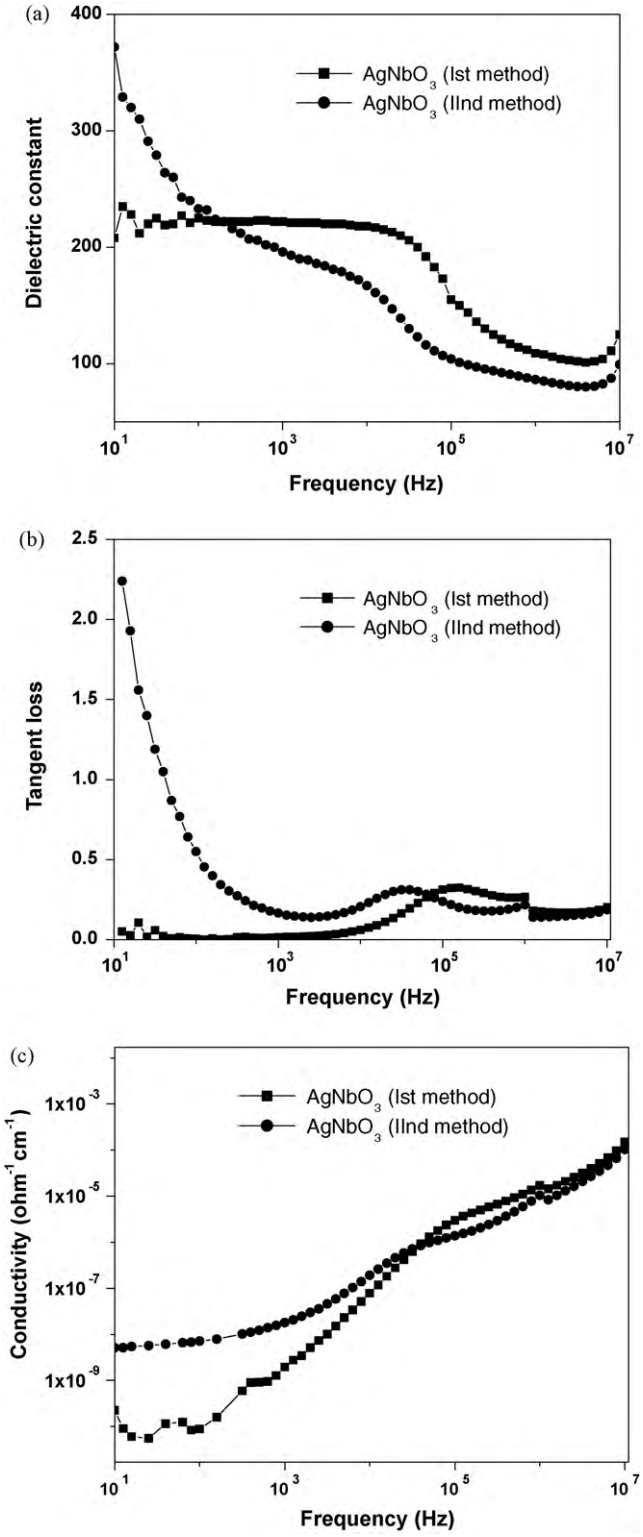


**Fig. 4.** Variation of dielectric constant, loss tangent (tan $\delta$) and conductivity ($\sigma$) with frequency in the frequency range 10 Hz to 10 MHz.

are larger which gives higher diffraction intensity. The crystallite size of the samples was calculated using Scherrer formula from the full width at half maximum (FWHM) of the highest intensity peak in the XRD pattern. The calculated crystallite sizes (XRD) for both the samples are given in Table 1.

Surface morphology and grain sizes of the prepared samples were studied by SEM technique. Fig. 2(a) and (b) shows the representative SEM micrographs for $AgNbO_3$ samples prepared by Ist and IInd method. The grains of different sizes are randomly distributed with large inter-granular porosity. The grain size ranges from few to several microns. The average grain size of $AgNbO_3$, prepared by both the methods was calculated. The grain sizes are

given in Table 1. The average grain sizes of $AgNbO_3$ prepared by second method, i.e. three-step sintering method were found larger compared to first method. The increase in grain sizes is due to the enhanced time and temperature of sintering in the second method.

The variations of dielectric constant ($K$), tangent loss ($\tan\delta$) and electrical conductivity ($\sigma$) of silver niobate ($AgNbO_3$) prepared by both the methods was monitored and compared. The frequency range chosen was from very low to very high (1 Hz to 10 MHz). The dielectric characteristics were found to be independent of preparation method. Fig. 3(a)–(c) shows the variation of dielectric constant ($K$), tangent loss ($\tan\delta$) and conductivity ($\sigma$) of silver niobate in the frequency range 1 Hz to 100 Hz at room temperature for the samples prepared by both methods. It is observed from Fig. 3 that the dielectric constant for silver niobate $AgNbO_3$ ceramic prepared by both methods slightly decreases with increasing frequency. It can be seen that the tangent loss ($\tan\delta$) also decreases as frequency increases. The conductivity slightly increases with increasing frequency in the measured frequency range 1 Hz to 100 Hz. The magnitude of dielectric constant, loss tangent and conductivity of the samples prepared by three-step sintering method was found higher compared to the samples prepared by calcination method.

Fig. 4(a)–(c) shows the variation of dielectric constant ($K$), tangent loss ($\tan\delta$) and conductivity ($\sigma$) with frequency at room temperature for $AgNbO_3$ prepared by two different methods in the frequency range from 10 Hz to 10 MHz. It was observed that the dielectric constant ($K$) as well as tangent loss ($\tan\delta$) decreases with increasing frequency in the measured frequency range of 10 Hz to 10 MHz. The dielectric constant ($K$) was found slightly higher for the sample prepared by calcination method compared to three-step sintering method in the frequency range 200 Hz to 10 MHz. The tangent loss ($\tan\delta$) was found smaller in the lower frequency range (10 Hz to 90 kHz) for the sample prepared by calcination method compared to three-step sintering method. In the higher frequency range 90 kHz to 10 MHz tangent loss ($\tan\delta$) for the sample prepared by calcination method has been found slightly more or approximately same. The conductivity ($\sigma$) increases as frequency increases in the frequency range 10 Hz to 10 MHz. It was observed that the increase in conductivity is more for the samples prepared by calcination method. The magnitude of conductivity of samples prepared by calcination (Ist) method has been found less in lower frequency range and more in the higher frequency range than that of samples prepared by three-step sintering (IInd) method.

## 4. Conclusions

Silver niobate, $AgNbO_3$ ceramic samples were prepared by solid-state reaction and sintering method. Sintering process was done by two different methods of calcination and three-step sintering. The sintered samples were investigated for phase and crystallinity by powder X-ray diffraction. The XRD results show that $AgNbO_3$ belongs to the orthorhombic structure at room temperature. The lattice parameters of $AgNbO_3$ system prepared by both the methods are found nearly same. The crystallite sizes for sample made by three-step sintering process are larger compared to those made by first method. The SEM results also support the larger grain sizes for the samples made by three-step sintering method. The dielectric constant ($K$), tangent loss ($\tan\delta$) and conductivity ($\sigma$) of silver niobate ($AgNbO_3$) prepared by both the methods were found mostly independent of preparation method.

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## References

[1] I. Levin, V. Krayzman, J.C. Woicik, J. Karapetrova, T. Proffen, M.G. Tucker, I.M. Reaney, Phys. Rev. B 79 (2009) 104113 (14 pp.).
[2] J. Fabry, Z. Zikmund, A. Kania, V. Petricek, Acta Cryst. C 56 (2000) 916–918.
[3] M. Valant, D. Suvorov, C. Hoffmann, H. Sommariva, Eur. Ceram. Soc. 21 (2001) 2647–2651.
[4] S. Duguey, R. Lebourgeois, C. Grattepain, J. Heintz, J.P. Ganne, Eur. Ceram. Soc. 27 (2007) 1171–1177.
[5] M. Valant, A.K. Axelsson, N. Alford, Eur. Ceram. Soc. 27 (2007) 2549–2560.
[6] O.P. Nautiyal, S.C. Bhatt, R.P. Pant, A.A. Bourai, P.K. Singh, R. Saxena, B.S. Semwal, Indian J. Pure Appl. Phys. 47 (2009) 282–288.
[7] A. Kania, J. Phys. D: Appl. Phys. 34 (2001) 1447–1453.
[8] O.P. Nautiyal, S.C. Bhatt, R.P. Pant, B.S. Semwal, Indian J. Pure Appl. Phys. 48 (2010) 357–362.
[9] O.P. Nautiyal, S.C. Bhatt, B.S. Semwal, Indian J. Pure Appl. Phys. 47 (2009) 719–724.
[10] A. Kania, S. Miga, Mater. Sci. Eng. B 86 (2001) 128–133.
[11] S. Wada, A. Saito, T. Hoshina, H. Kakemoto, T. Tsurumi, C. Moriyoshi, Y. Kuroiwa, Jpn. J. Appl. Phys 45 (2006) 7389–7396.
[12] O.P. Nautiyal, S.C. Bhatt, J. Alloys Compd. (submitted for publication).
[13] S. Wada, A. Saito, T. Hoshina, H. Kakemoto, T. Tsurumi, C. Moriyoshi, Y. Kuroiwa, Ferroelectrics 346 (2007) 64–71.
[14] A. Saito, S. Uraki, H. Kakemoto, T. Tsurumi, S. Wada, Mater. Sci. Eng. B 120 (2005) 166–169.