SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF VANADIUM DOPED SODIUM NIOBATE [Na (Nb$_{1-x}$V$_x$) O$_3$, x = 0.30]

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ABSTRACT

Transition metal oxides show various physical properties and have a good basic physics because of the complex interactions between their charges, orbital, spin and lattice degree of freedoms. The unusual properties of transition metal oxides are due to the unique nature of d-electrons. Here, we reports the synthesis of NaNbO$_3$, NaVO$_3$ and its solid solution of the type, Na(Nb$_{1-x}$V$_x$)O$_3$, for x=0.30 by conventional solid state ceramic method to study the improvements in properties of the resulting materials. The phase purity of the samples (NaNbO$_3$, NaVO$_3$ and Na(Nb$_{1-x}$V$_x$)O$_3$) is confirmed by XRD analysis. The structural confirmation is also investigated using FTIR and Raman spectroscopy.

Keywords: Solid State Ceramic Method, XRD, Micro-Raman Analysis, FTIR.

I. INTRODUCTION

Perovskite family of oxides having ABO$_3$ type structure have been widely studied during the last few decades because of their importance in science and technology [1- 3]. From the scientific point of view, the importance of the study of ferroelectric materials comes from (i) the several phase transitions undergone by the materials, (ii) the mechanisms associated with them and (iii) the diverse ways of modeling and explaining the many phases and new theoretical approaches, such as the recently discovered polarization rotation path under electric fields [4, 5].

Sodium Niobate (NaNbO$_3$) is antiferroelectric at room temperature. NaNbO$_3$ exhibits a complex sequence of structural phase transition as a function of temperature. On cooling, NaNbO$_3$ undergoes the following series of phase transformations: 914 > T > 848 K, tetragonal T2 phase; 848 > T > 793 K, orthorhombic T1 phase; 793 > T > 753 K, orthorhombic S phase; 753 > T > 646 K, orthorhombic R phase; 646 > T > 163 K, orthorhombic P phase; and T < 163 K, rhombohedral N phase. In the rhombohedral phase, the crystal is ferroelectric and in the other regions, T < 914 K, NaNbO$_3$ is antiferroelectric [6- 8]. It exhibits a transition from the paraelectric to the antiferroelectric (AFE) and then to the ferroelectric (FE) phase and therefore is of particular interest from the point of view of sequence of phase transitions. At room temperature, NaNbO$_3$ makes a transition to the FE phase under modest electric field. This property makes it important for various applications including high-density optical data storage. NaNbO$_3$ has excellent non-linear optical properties, good photo-catalytic properties [9] and finds significant applications as hologram recording materials [10]. On other hand, Sodium meta-vanadate (NaVO$_3$) is ferroelectric below 380^{0}C [11]. At atmospheric pressure and room temperature, NaVO$_3$ can exist in two crystal modifications: stable monoclinic α-phase (space group Cc) and meta-stable

orthorhombic β phase (space group Pnma). After heating to 405°C, the meta-stable β-phase transforms irreversibly into α-phase [12-14].
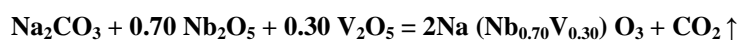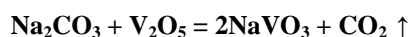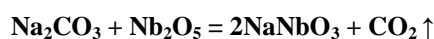
In this paper, we report the synthesis of $NaNbO_3$, $NaVO_3$ and its solid solution of the type, Na $(Nb_{1-x}V_x)$ O_3, for x=0.30 by conventional solid state ceramic method to study the structural properties of resulting materials. The phase purity of the samples ($NaNbO_3$, $NaVO_3$ and $Na(Nb_{1-x}V_x)O_3$) is confirmed by XRD analysis. The structural studies are also investigated by FTIR and Raman spectroscopy.

II. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

Polycrystalline $NaNbO_3$, $NaVO_3$ and solid solution of both ($Na(Nb_{1-x}V_x)O_3$), were synthesized by the conventional solid-state reaction method using Na_2CO_3, Nb_2O_5, V_2O_5 (all chemicals employed in the synthesis are of analytical grade and were used without any further purification) reagents as starting materials. These reagents were carefully weighed in suitable stoichiometric amounts and grinded separately in acetone medium for 5 hours using an agate mortar. The homogeneously mixed powders were calcined at different temparatures (for $NaNbO_3$ 1100^0C; $NaVO_3$ 700^0C; for solid solution 900^0C) for 4 hours in a furnace with controlled heating rate in air medium. The calcined powders were again mixed and grinded for 1 hour to decrease the particle size and mixing of any unreacted materials during calcination. Fine calcined powder was pressed into disc-shaped pellets at an iso-static pressure of 4 ton/square inch. Poly Vinyl Alcohol (PVA) was used as a binder. The pellets were sintered in presence of air using controlled heating and cooling rates in a programmable furnace; each sample was fired first up to 300°C where temperature was raised from room temperature in 2 hours and the temperature was kept constant for half an hour to remove the binder and then it was again raised to 500°C within 3 hours and finally to 900°C, in another 3 hours., The sintered pellets and calcined powders both are subjected for characterization to X-ray powder diffraction analysis to check the formation of single phase material.

The reactions taken place during calcination and sintering are as following:

$$Na_2CO_3 + Nb_2O_5 = 2NaNbO_3 + CO_2 \uparrow$$

$$Na_2CO_3 + V_2O_5 = 2NaVO_3 + CO_2 \uparrow$$

$$Na_2CO_3 + 0.70\ Nb_2O_5 + 0.30\ V_2O_5 = 2Na\ (Nb_{0.70}V_{0.30})\ O_3 + CO_2 \uparrow$$

2.2 Characterization techniques

The XRD of as calcined samples as well as sintered pellets were taken by Rigaku Smart Lab (Japan) X-ray diffractometer with $CuK_{\alpha 1}$ (λ= 0.154056 nm) radiation at room temperature. The data was collected with a scanning speed of 4^0 per minute with a step size of 0.06^0 over the angular range 2θ ($20^0 < 2\theta < 80^0$) generating X-ray by 40 kV and 75 mA power settings. Raman spectra of sintered pellets were taken by STR-500 Micro-Raman Spectrometer (Japan) at room temperature. FTIR spectra were taken by Shimadsu 8400S (Japan), KBr powder taken as the reference material and the sample to KBr ratio is ~ 95:05.

III. RESULTS AND DISCUSSIONS

3.1 XRD Analysis

X-ray Diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, grain size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases. Figure 1 shows the XRD pattern of different samples. $NaNbO_3$ have distorted perovskite structure [15]; it has orthorhombic structure with space group Pbma (57) [PDF card no. 19-122]. $NaVO_3$ have a monoclinic structure with a space group Cc [PDF card no.: 27-828] [16, 17]. There are some extra/impurity phase present in $NaVO_3$ XRD pattern. Solid solution of both, $Na(Nb_{1-x}V_x)O_3$ has an orthorhombic structure.

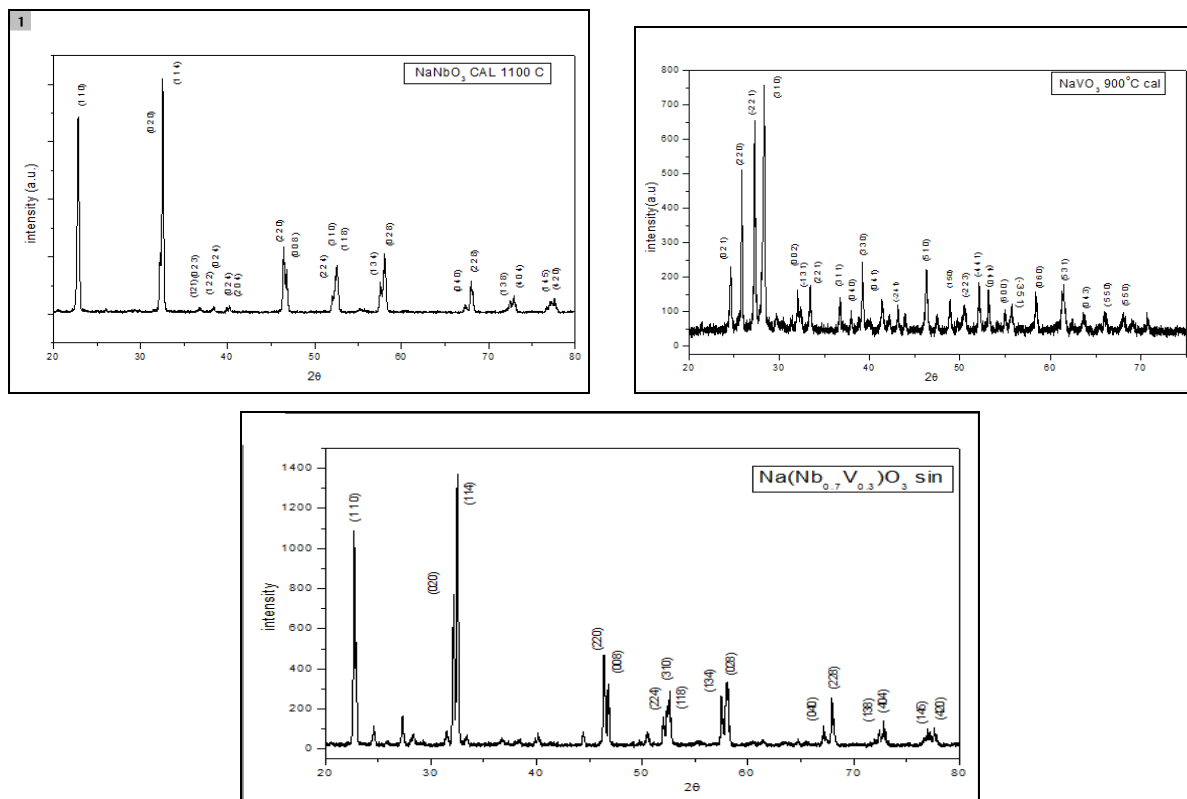**Figure 1: Room temparature powder XRD of $NaNbO_3$, $NaVO_3$, $Na (Nb_{0.70}V_{0.30}) O_3$**

3.2 FTIR Analysis

FTIR spectra of prepared samples are shown in figure 2. The absorption peak in the region 520-840 cm^{-1} belongs to Nb-O stretching vibration in NbO_6 octahedra. For $NaVO_3$ powder sample, the IR absorption bands at low wave number region are well matched with the Raman scattering data; the V–O stretching vibration bands at the 950–880 cm^{-1} region and the O–V–O asymmetric vibration band at about 560 cm^{-1}. For solid solution, all the indexed peaks have also a good agreement with reported data [18-20].
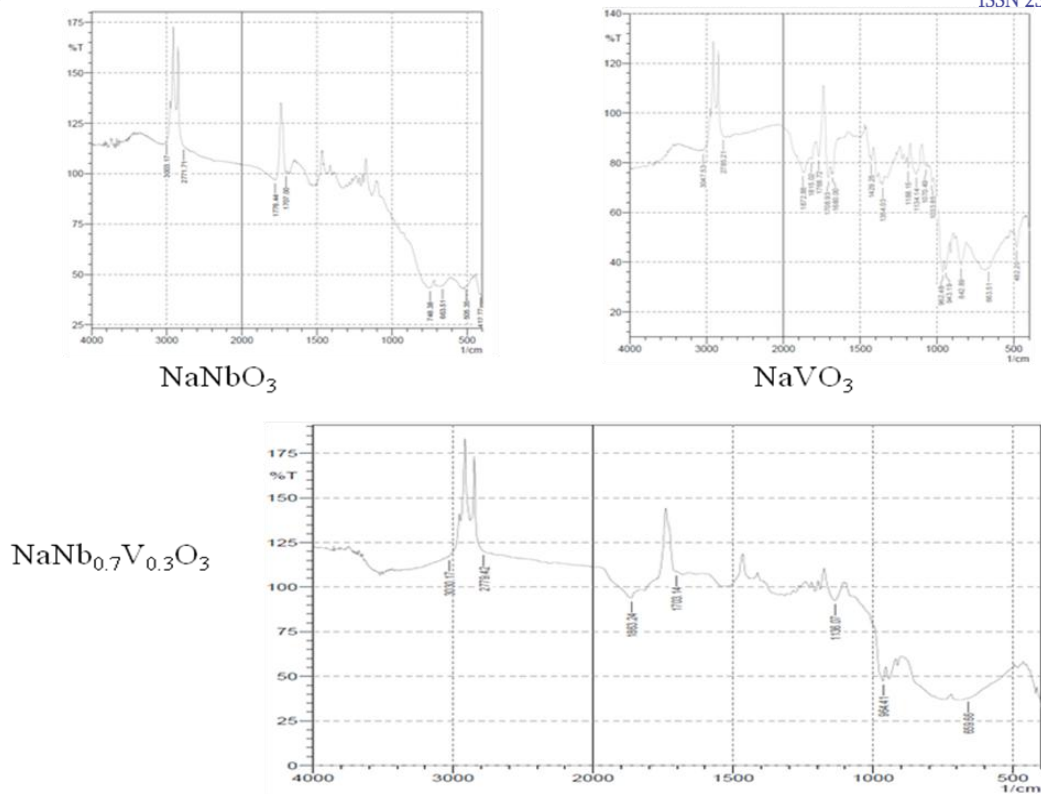
Figure2: FTIR of calcined samples

3.3 Raman Analysis

Raman scattering spectrum of sodium vanadate ($NaVO_3$) is shown in figure-3. The Raman peaks at 956, 941, and 920 cm^{-1} are assigned to the stretching vibrations (v_s) of the V–O (1) and V–O (2), which are well matched with the published data [9,15]. The bands at 805 and 635 cm^{-1} are assigned to the asymmetric stretching (v_{as}) of the O–V–O, while the band at 510 cm^{-1} is assigned to the symmetric stretching (v_s) of the O–V–O. The Raman peaks of the low-frequency region (lower than 400 cm^{-1}) may be related to the external vibrations, i.e. crystal lattice translational (T) and rotational (R) modes [20]. The peak at the wave number 125 cm^{-1} is related to NbO_6 rotation. The spectral region (wave number 100 –1100 cm^{-1}) presented in Fig. 3 has bands associated with the v_4, v_2, v_1 and v_3 vibrations of the NbO_6 group. The band assigned to $v_5 + v_1$ is a combination tone of two fundamentals. The bands corresponding to v_4 (NbO_6) have very low intensity but it was possible to observe them at all temperatures investigated. The same is true of the v_3 (NbO_6) band, which was observed at low temperatures as a very low-intensity band and at high temperatures as a shoulder on the v_1 band [21-22].
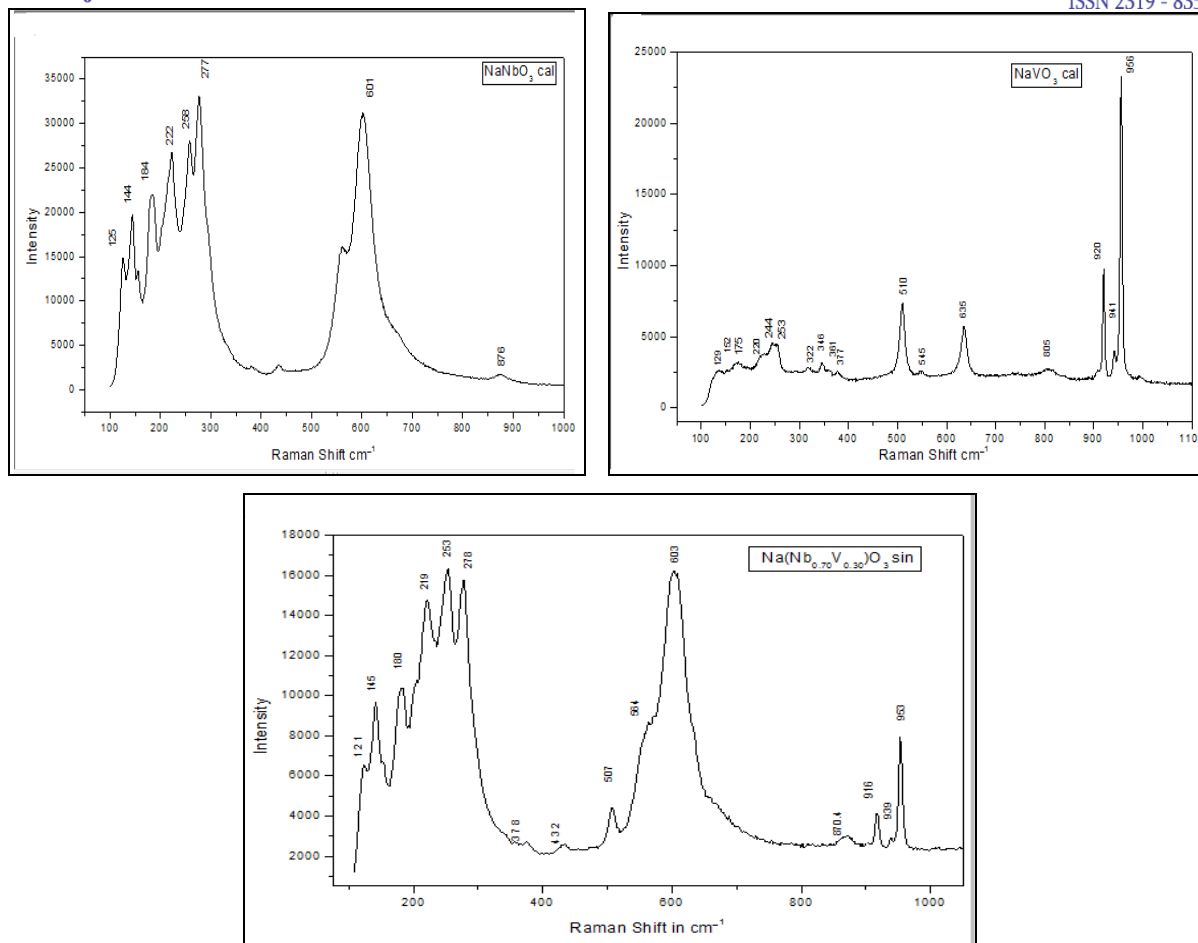
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Figure 3: Room temparature RAMAN spectra of synthesized materials

IV. CONCLUSIONS

In this present paper, we have successfully synthesized the compound $NaNbO_3$, $NaVO_3$ and solid solution of both by using Na_2CO_3, V_2O_5 and Nb_2O_5 reactants. Transition metal ion, Vanadium (V) doping (30%) is made at Nb site. From XRD analysis, we mach the structure of $NaNbO_3$ is orthorhombic structure. $NaVO_3$ is monoclinic structure and solid solution, $Na(Nb_{1-x}V_x)O_3$ is also orthorhombic. From Raman analysis of $NaVO_3$, $NaNbO_3$ Vandium doped Sodium Niobate [Na $(Nb_{1-x}V_x)O_3$, x=0.30], we have indentified all intense observed peaks and explained the every molecular vibrations. FTIR and RAMAN studies have a good agreement with previously reported data in literature.

V. ACKNOWLEDGEMENTS

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