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Ferroelectricity in the $x\text{Ag}_2\text{Nb}_4\text{O}_{11}$ – $(1\text{-}x)\text{Na}_2\text{Nb}_4\text{O}_{11}$ solid solution

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Abstract

Compositions in the $(\text{Ag}_x\text{Na}_{1-x})_2\text{Nb}_4\text{O}_{11}$ solid solution have been prepared by a conventional solid state method. Composites containing $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ have been shown to be ferroelectric and the Curie temperature shown to decrease from 149 °C at $x = 1$ to 62 °C at $x = 0.7$. Room-temperature compositions with $x \leq 0.7$ are monoclinic, while those with $x \geq 0.8$ are rhombohedral with structures consistent with the relevant end-members. At $x = 0.75$, the structure was mainly rhombohedral but with coexistence of the monoclinic structure, indicating the proximity of a phase boundary.

Text:

The Ag_2O–Nb_2O_5 binary system is rich in phases, with at least 5 discrete phases known to form.[1–3] Of these, AgNbO_3 perovskite is the most widely studied, principally for its potential role in lead-free piezoelectrics,[4] for its dielectric properties[5] and unusual phase transitions.[6] This leaves a large number of related materials whose structures and properties are largely unknown. $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ is one such material known to form as a secondary phase when making AgNbO_3 due to Ag^+ loss,[6] while the related $\text{Ag}_2(\text{Nb}_{0.5}\text{Ta}_{0.5})_4\text{O}_{11}$ is a prominent secondary phase when forming $\text{Ag}(\text{Nb}_{0.5}\text{Ta}_{0.5})\text{O}_3$ thin films.[7] Single phase $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ and $\text{Na}_2\text{Nb}_4\text{O}_{11}$ have recently been made and studied.[8] The structure of $\text{Na}_2\text{Nb}_4\text{O}_{11}$ was originally refined in the centrosymmetric space group $C2/c$[9] but a model with the non-centrosymmetric space group Cc has also been proposed.[8] Recently, $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ was found to have a structure similar to the mineral natrotantite, $\text{Na}_2\text{Ta}_4\text{O}_{11}$ ($R\bar{3}c$)[10,11] but the demonstrated absence of a centre of symmetry results in space group $R3c$ and the possibility of a ferroelectric structure.[12] In this work, the results of forming a solid solution between $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ and $\text{Na}_2\text{Nb}_4\text{O}_{11}$ are explored using x-ray diffraction (XRD) and second harmonic generation (SHG).

Powder samples in the $(\text{Ag}_x\text{Na}_{1-x})_2\text{Nb}_4\text{O}_{11}$ series were made using a conventional solid-state processing route. Na_2CO_3 (BDH, 99 %), Ag_2O (Alfa Aesar, 99+ %) and Nb_2O_5 (Alfa Aesar, 99.9985 %) were weighed in stoichiometric quantities and ball-milled in propan-2-ol for ~ 24 h. The resultant mixture was dried at 70 °C, ground using a pestle and mortar and passed through a 250 μm sieve. The powders were then reacted at 775 – 800 °C in a lidded alumina crucible for 2 h, using a heating rate of 5 °/m and fast furnace cooling. XRD was performed on the powders using a PANalytical X'Pert Pro MPD with a curved Johansson monochromator resulting in focused $\text{CuK}\alpha_1$ radiation. The process of making ceramics of $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ causes the material to decompose into AgNbO_3 and AgNb_3O_8, a tungsten bronze phase.[2] In order to make dense bodies, $\text{Ag}_2\text{Nb}_4\text{O}_{11}$ and $\text{Na}_2\text{Nb}_4\text{O}_{11}$ powders were mixed with M-Bond 610 epoxy, centrifuged[13] and cured at 100 °C for 4 hours with a heating rate of 0.5 °/m. The resulting hard composites were thinned, silver conductive paint (RS components) used to add electrodes and poled for 10 minutes at 6 kV/mm in silicone oil. Measurements of d_{33} were performed with a YE2730A d_{33} meter (APC International, Ltd). SHG was performed using a set-up described in greater detail elsewhere.[12] A neodymium-doped yttrium aluminium garnet (Nd-YAG) laser generated an infrared beam ($\lambda = 1064$ nm)

directed at powder samples and the resulting second harmonic was filtered and its intensity measured by a photomultiplier and recorded by an oscilloscope. Samples were heated and cooled at 30 °/h and did not show signs of having decomposed while exposed to the laser.

All powders were white but, with the exception of $x = 0$, turned purple when exposed to sufficiently intense sunlight, x-rays or laser, presumably due to reduction of Ag^+ to Ag metal as with silver halides. XRD (figure 1a) showed for all compositions except $x = 1$ the presence of a small amount of secondary phase indicated by the appearance of a peak at ~ 22.5 °2θ. This is the strongest peak corresponding to the presence of the ferroelectric tungsten bronze-structured material $Na_{13}Nb_{35}O_{94}$,[14,15] and attempts to remove this phase by adding excess Na_2CO_3 to the batches or by varying the reaction temperature had no significant effect. No evidence of Ag metal was observed. Movement of the peaks to higher 2θ with decreasing x indicates reduction in volume, as expected, given that the Na^+ ion is smaller than the Ag^+ ion.[16] XRD showed that all compositions with $x \leq 0.7$ had structures consistent with monoclinic $Na_2Nb_4O_{11}$ and compositions with $x \geq 0.75$ had structures consistent with rhombohedral $Ag_2Nb_4O_{11}$, although the data for $x = 0.75$ show a small proportion of the monoclinic phase in coexistence with the rhombohedral phase, which implies the existence of a phase boundary between the two structural variants at $x \approx 0.75$. The monoclinic and rhombohedral structures are related by the identities:

$$[100]_M \equiv [\bar{1}10]_R \tag{1}$$

$$[010]_M \equiv [110]_R \tag{2}$$

$$[001]_M \equiv \tfrac{1}{3}[1\bar{1}1]_R \tag{3}$$

(where the rhombohedral cell is described on the hexagonal setting). The splitting of the $\{030\}_R$ peak to $\{60\bar{2}\}_M$ and $\{\bar{3}31\}_M$ peaks is shown in figure 1b as an illustration of the distortion encountered as a function of composition. It can be seen that the monoclinic peak splitting remains largely constant for $x \leq 0.75$ suggesting that, unlike a perovskite, the natrotantite structure has limited means to improve the accommodation of ions that are not of ideal size. The fact that the structure contains planes of edge-sharing NbO_7 polyhedra means that there cannot be a simple in-plane tilting mechanism to effect small reductions in volume. The relationship between the rhombohedral and monoclinic structures is illustrated in figure 2.

Prior to poling, the $Ag_2Nb_4O_{11}$ composites did not have a measurable d_{33}, but after poling, a reproducible d_{33} of of 3.4 (2) pC N^{-1} was obtained. This value could be reversed by reversing the direction of the electric field, but decayed slowly over time, indicating a significant conductivity within the composite. The ability to switch the polarization of this composite proves that the material is ferroelectric. By contrast, the $Na_2Nb_4O_{11}$ composites gave a d_{33} value of zero both before and after poling. This shows that the resin is not responsible for piezoelectricity, that the $Na_{13}Nb_{35}O_{94}$ secondary phase is not present in sufficiently large quantities to have a measurable effect on the overall piezoelectricity of the composite and that $Na_2Nb_4O_{11}$ does not appear to be ferroelectric and is thus more likely to be the centrosymmetric space group $C2/c$ than the non-centrosymmetric space group Cc.

A particularly strong second harmonic signal was obtained at room temperature for samples with $x \geq 0.75$, but a much weaker signal obtained for all other compositions. At $x = 0.7$ a weak signal at room temperature was recorded, but became particularly strong at ~ 40 °C. It is here proposed that the strong signal corresponds to the ferroelectric $R3c$ phase and the loss of this signal occurs at the Curie temperature, T_C. Figure 3a shows the loss of the second harmonic for compositions $x \geq 0.7$. By modeling the data above and below T_C each with a straight line, T_C is determined as the temperature at which the lines cross (Table I, Figure 3b). It can be seen that the progressive substitution of Ag for Na reduces T_C up to the phase boundary. The composition $x = 0.7$ is monoclinic at room temperature, yet the strong

second harmonic encountered at ~ 40 °C may indicate that it goes through a phase transition to the rhombohedral $R3c$ structure slightly above room temperature, before going through another phase transition to $R\bar{3}c$ at ~ 62 °C. Compositions $x < 0.7$ had a weak second harmonic signal that did not display any obvious phase transitions. The additional evidence of small amounts of a ferroelectric secondary phase makes it impossible to reach any conclusions about the existence of ferroelectricity or even pyroelectricity across the monoclinic phase field.

In conclusion, powders have been made in the $(Ag_xNa_{1-x})_2Nb_4O_{11}$ solid solution. Those with compositions $x \leq 0.7$ have been shown to be monoclinic, consistent with the $Na_2Nb_4O_{11}$ structure, which appears non-polar. Those with compositions $x \geq 0.8$ have been shown to be rhombohedral $R3c$, consistent with the $Ag_2Nb_4O_{11}$ structure. At $x = 0.75$, the structure was predominantly $R3c$, with some coexistence of the monoclinic phase, indicating the proximity of a phase transition to this composition. An $Ag_2Nb_4O_{11}$ composite was poled and shown to be piezoelectric, reversible by an external field, proving that this material is ferroelectric and SHG showed that ferroelectricity is encountered in samples with compositions $x \geq 0.7$. A phase transition sequence monoclinic $- R3c - R\bar{3}c$ over the range 20 $- 62$ °C is postulated for $x = 0.7$.

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Tables:

Table I: T_Cs for $(Ag_xNa_{1-x})_2Nb_4O_{11}$ compositions obtained from SHG. The reproducibility of the temperatures is ± 5 °C.

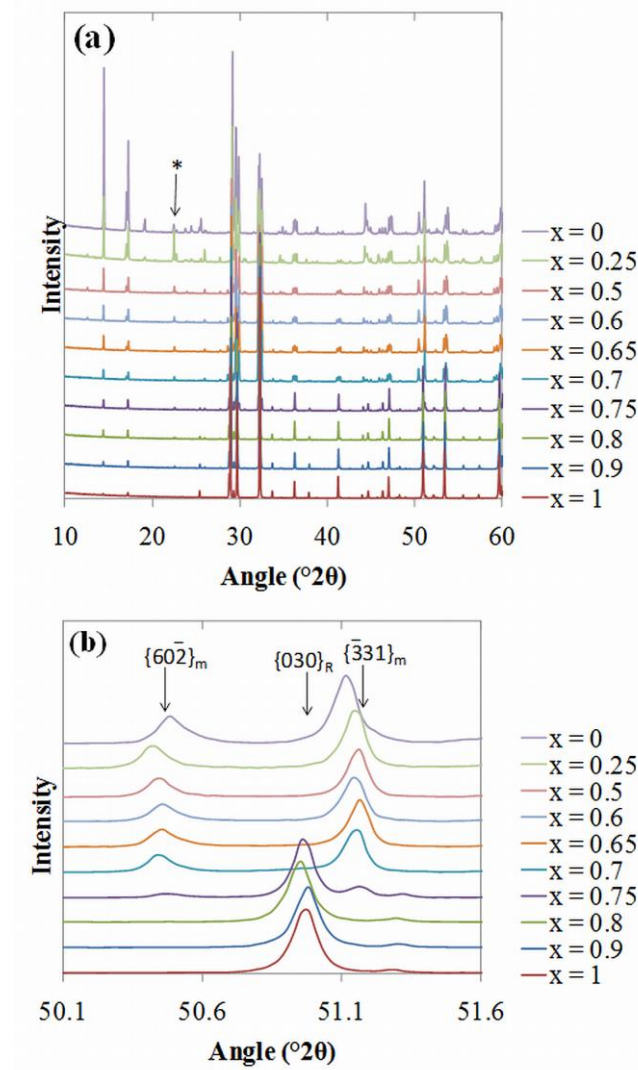| Composition, x	T_C (°C)
1	149
0.9	121
0.8	86
0.75	81
0.7	62

Figures:

Figure 1: XRD data for all compositions showing (a) the evolution of peaks throughout the series (a peak indicating the presence of $Na_{13}Nb_{35}O_{94}$ is indicated by *) (b) splitting of the $\{030\}_R$ rhombohedral peak into the doublet of peaks $\{60\bar{2}\}_M$ and $\{\bar{3}31\}_M$ on transforming to the monoclinic system.
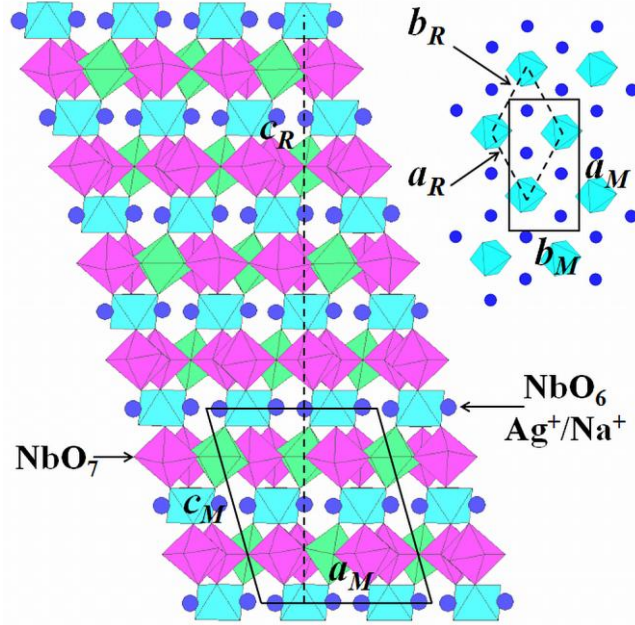
Figure 2: Illustration of the natrotantite crystal structure indicating the relationship between the monoclinic cell (bold lines) and the rhombohedral cell (dashed lines). Alternate layers of NbO_7 polyhedra and NbO_6 polyhedra with Na^+/Ag^+ positions are indicated.
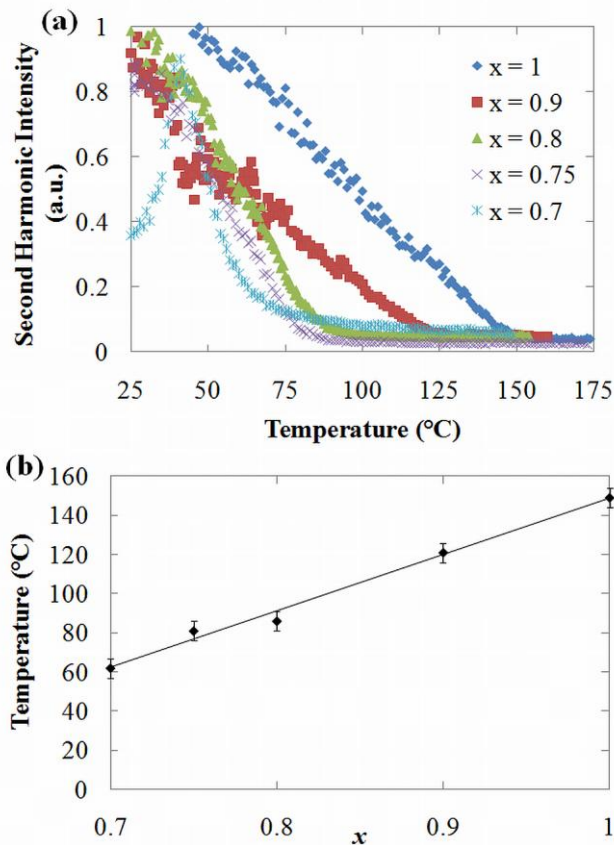

Figure 3: (a) Raw SHG data for compositions $x \geq 0.7$ (b) T_Cs obtained from SHG data.