

Raman Spectroscopy of $\text{Na}_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{Nb}_{2-x}\text{M}_x\text{O}_{6-x}(\text{OH})_x \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Ti}, \text{Hf}$) Ion Exchangers

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The Raman spectra of Sandia Octahedral Molecular Sieves $\text{Na}_2\text{Nb}_{2-x}\text{M}_x\text{O}_{6-x}(\text{OH})_x \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Ti}, \text{Hf}$; $x \leq 0.2$) (SOMS–Ti and SOMS–Hf) and their parent compound $\text{Na}_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}$ (SOMS) were measured between 24 °C and 600 °C. The spectra of all three materials as well their variations with temperature are almost identical, which indicates that the M^{4+} for Nb^{5+} disordered substitution has little effect on the structure of the niobate framework. The annealing above 250 °C results in dehydration reflected in the Raman spectra by disappearance of water-related bands at $\sim 1700 \text{ cm}^{-1}$ and $3100\text{--}3400 \text{ cm}^{-1}$ and irreversible changes of some Raman line parameters. As a whole, however, the spectral changes in the frequency range, corresponding to internal oxygen vibrations, are rather modest in contrast to the drastic changes of the X-ray diffraction patterns. This shows that although the SOMS structure rearranges in the dehydrated phase, the basic constituting elements, NbO_6 octahedra and Na-centered polyhedra, remain practically unchanged. At further annealing above ~ 500 °C the Raman spectrum transforms irreversibly into a spectral structure consisting of three broad bands centered (at 24 °C) at 232, 600, and 876 cm^{-1} , while the X-ray pattern indicates transformation to a perovskite-like structure. We argue that the Raman spectrum in this case reflects the density of vibrational states of a strongly disordered oxygen sublattice.

1. Introduction

Sandia Octahedral Molecular Sieves (SOMS–M) $\text{Na}_2\text{Nb}_{2-x}\text{M}_x\text{O}_{6-x}(\text{OH})_x \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Ti}, \text{Hf}, \text{Zr}, \dots$) exhibit high selectivity for A^{2+} for Na^+ ion exchange ($\text{A} = \text{Ba}, \text{Sr}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}, \text{Pb}$).^{1,2} This property can potentially be used to sequester and immobilize hazardous divalent metals from radioactive and/or industrial waste. Such applications are highly appealing, and a better understanding of properties of SOMS–M and their variants under different treatments are of definite interest. Recently, a detailed study of structural and ion-exchange properties of $\text{Na}_2\text{Nb}_{2-x}\text{M}_x\text{O}_{6-x}(\text{OH})_x \cdot \text{H}_2\text{O}$ [$\text{M} = \text{Ti}, \text{Zr}$; ($0.04 \leq x \leq 0.40$)] was performed by means of X-ray powder diffraction, infrared spectroscopy, thermogravimetric analysis, and NMR.² At room temperature the structure of SOMS is monoclinic (space group $C2/c$, #15, $Z = 8$), containing double chains of Nb/Ti centered octahedra along the b -axis connected to two layers of six-coordinated Na-centered polyhedra parallel to the xy -plane. Another square-planar Na-site, located in the channels between the $(\text{Nb}/\text{Ti})\text{O}_6$ chains, is bonded to two water molecules and two framework oxygens. Upon annealing above 250 °C, dehydration occurs and a still unidentified intermediate phase is formed in a vacuum.² Further annealing results in the formation of a perovskite-like structure above 500 °C.

Raman spectroscopy is an efficient tool for obtaining information on the local atomic structure and its variations under different treatments. Raman spectroscopy has been very useful

in understanding both zeolite crystalline structures and the effects of metal-dopant on framework activity in a number of studies focused on silica-based zeolites.^{3–5} As a rule, a Raman active mode involves motions of mainly one type of atom. The frequency and polarization properties of a given Raman mode are determined by the atomic site symmetry, distances to the nearest neighbors and the type of vibrations (stretching, bending, or rotational). Any structural change results in changes in Raman line parameters. Structural disorder is also reflected in the Raman spectra by line broadening and activation of otherwise Raman-forbidden vibrations.

This paper presents the results of Raman study of $\text{Na}_2\text{Nb}_{1.8}\text{Ti}_{0.2}\text{O}_{5.8}(\text{OH})_{0.2} \cdot \text{H}_2\text{O}$ (SOMS–Ti), $\text{Na}_2\text{Nb}_{1.9}\text{Hf}_{0.1}\text{O}_{5.9}(\text{OH})_{0.1} \cdot \text{H}_2\text{O}$ (SOMS–Hf) and their parent compound $\text{Na}_2\text{Nb}_2\text{O}_6 \cdot \text{H}_2\text{O}$ (SOMS) between 24 °C and 600 °C. Over the whole temperature range, the Raman spectra of each of SOMS–Ti, SOMS–Hf, and SOMS are practically the same at a given temperature—an indication that the substitution of Ti or Hf for Nb does not result in noticeable structural differences. The dehydration results in structural rearrangements and increasing disorder but the main constituent elements—the NbO_6 octahedra and the Na-centered polyhedra—remain practically unchanged. The drastic changes of the Raman spectra above 500 °C provide evidence for an irreversible transition to a perovskite-like phase with a strongly disordered oxygen sublattice.

2. Samples and Experimental Section

The samples were prepared by hydrothermal treatment of sol mixtures containing water, sodium hydroxide, and hydrolyzed metal (Nb, Ti, Hf) alcohohydrides according to the following procedures: SOMS: 0.65 g of ethyl acetate was mixed with

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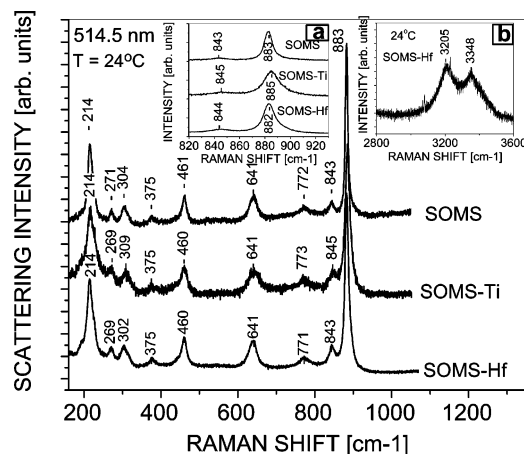


Figure 1. Raman spectra of SOMS, SOMS-Ti, and SOMS-Hf at 24 °C.

3.28 g of NaOH in 10 mL of DI H₂O to a clear liquid. Then 1.35 g of NbCl₅ was added, stirred, and the entire mixture was added to a Parr reactor, heated at 443 K for 24 h. *SOMS-Hf*: 1.27 g of Nb(OC₂H₅)₅ was mixed with 0.41 g of Hf(OC₂H₅)₄. The mixture was added to 2.46 g of NaOH and 10 mL of H₂O. After mixing, the reactants were heated in a Parr reactor at 443 K for 9 days; 0.954 g of product was recovered by vacuum filtration. *SOMS-Ti*: the synthesis is described in detail in reference 2. The elemental content was confirmed by elemental analysis (Galbraith Laboratories, Inc.) and by electron microprobe analysis (JEOL JXA8600).

The X-ray diffraction patterns were determined using a Siemens D5000 powder diffractometer with Cu K α X-ray radiation generated at 40 kV accelerating voltage with an operating current of 30 mA. The data were collected on-line at a scan rate of 0.02° 2 θ per second.

The Raman spectra were measured under a microscope using a 50 \times or 100 \times objective to focus the incident excitation laser radiation into a spot 1–2 μ m or 2–3 μ m diameter, respectively, and to collect the scattered light. The spectra were obtained using a Jobin Yvon HR640 spectrometer equipped with notch filter(s) and a liquid nitrogen cooled CCD detector. Both 632.8 and 514.5 nm laser lines were used for excitation; the spectra being practically the same. For high-temperature measurements, the samples were heated in air in the heating stage TR600 (Lincam).

3. Results and Discussion

In the monoclinic C2/c structure, all atoms occupy noncentrosymmetrical sites and their vibrations are Raman active. From symmetry considerations, a total of 81 (40A_g + 41B_g) Raman modes are allowed.⁶ Figure 1 shows the Raman spectra of SOMS, SOMS-Ti, and SOMS-Hf at 24 °C between 160 and 1000 cm⁻¹. The positions, widths, and relative intensities of the Raman lines in all three spectra are very close: an indication that the substitution of Ti⁴⁺(Hf⁴⁺) for Nb⁵⁺ and presence of OH⁻ affect only weakly the structure of SOMS. The left inset in Figure 1 illustrates the small shift of the 883 cm⁻¹ peak of SOMS to 885 cm⁻¹ (SOMS-Ti) and 882 cm⁻¹ (SOMS-Hf), respectively. The peak at 304 cm⁻¹ (SOMS) shifts even stronger to 309 cm⁻¹ (SOMS-Ti) and 302 cm⁻¹ (SOMS-Hf). The shift directions are consistent with an expected increase or decrease of vibrational frequency upon substitution for Nb of a lighter (Ti) or a heavier (Hf) metal, respectively. An exact assignment of all experimentally observed Raman lines between 200 and 900 cm⁻¹ to definite atomic vibrations cannot be done at this

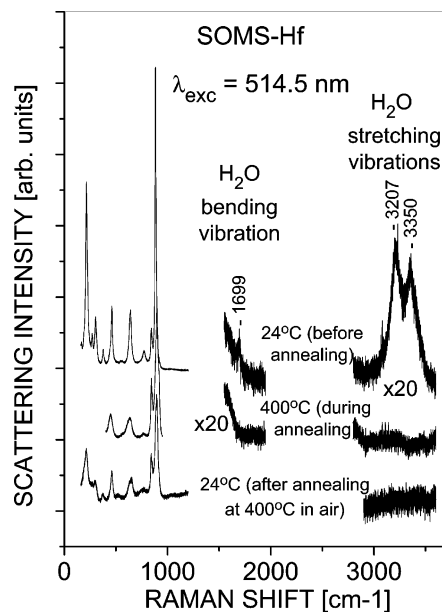


Figure 2. Raman spectra of SOMS-Hf at 24 °C (before annealing), 400 °C (during annealing), and 24 °C (after annealing at 400 °C).

stage. On the basis of mass and bond length considerations, however, it is reasonable to assign most of these lines to modes involving mainly vibrations of oxygen atoms. The stretching-type modes have higher frequency than the bending and rotational ones. Therefore with definite certainty, the Raman line of highest frequency in this range (884 cm⁻¹) corresponds to stretching vibrations along the shortest bonds Nb–O \approx 1.8 Å, i.e., to the internal stretching vibrations of NbO₆ octahedra. The much weaker bands related to bending and stretching vibrations of water at \sim 1700 cm⁻¹ and 3207/3350 cm⁻¹, respectively, are shown in Figure 1 (right insert) and Figure 2.

In Figure 2 are compared the Raman spectra SOMS-Hf at 24 °C (before annealing), 400 °C (during annealing), and 24 °C (after annealing at 400 °C). As expected, due to dehydration between 250 and 300 °C the water bands disappear. Simultaneously some irreversible changes occur in the lower energy part of the spectrum occur. Most noticeable are the broadening and hardening of the line near 883 cm⁻¹ and strong reduction of the 271 cm⁻¹ line intensity. This is illustrated in Figure 3 for the example of SOMS-Ti. The variations with temperature of the position and width of the 885 cm⁻¹ line of SOMS-Ti are shown in Figure 4.

X-ray diffraction patterns of SOMS-Ti determined at different temperatures in vacuo² show that three different crystal structures pertain over the temperature range 25–600 °C. The low-temperature SOMS changes to an “intermediate” phase at a temperature near 250 °C, and that undergoes a transition to the perovskite phase near 500 °C. The X-ray pattern determined for the intermediate phase has diffraction peaks corresponding to d = 6.35, 3.57, and 3.14 Å, none of which overlap with any diffraction peaks of SOMS or perovskite. We determined X-ray diffraction patterns for three samples: (a) without annealing, (b) after annealing in air at 300 °C for 6 h, and (c) after annealing in air at 600 °C for 6 h. Figure 5 compares these three patterns for SOMS-Ti and indicates the positions of the three peaks named above observed for the intermediate phase during annealing in vacuo. None of the three diffraction patterns determined by us has peaks at these positions. Furthermore, the X-ray patterns of the starting (a) and intermediate (b) samples are drastically different. This is in marked contrast with the temperature-dependent Raman spectra, which exhibit only

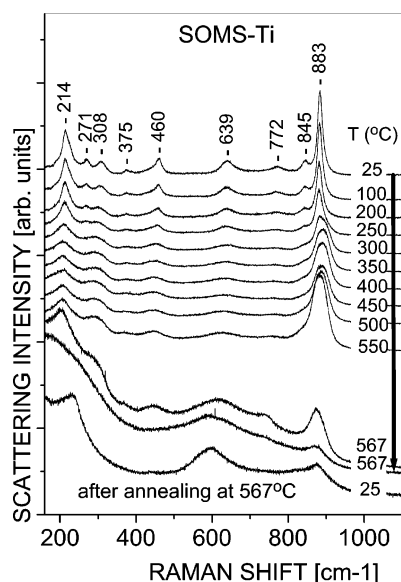


Figure 3. Variations with temperature of the Raman spectra of SOMS-Ti.

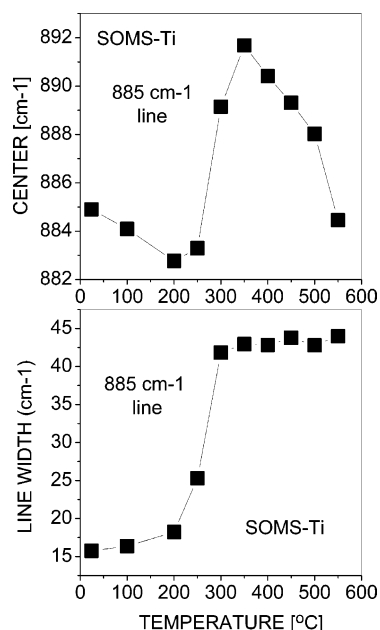


Figure 4. Variations with T of the position and line width of the Raman line at 885 cm^{-1} (SOMS-Ti).

moderate changes upon dehydration. This can be explained by the fact that the X-ray diffraction pattern and Raman spectra reflect different structural elements. X-ray diffraction gives an indication of long-range order, rather than short-range periodicity, and does not really give local atomic symmetry information. Raman spectroscopy is an experimental technique sensitive to the local atomic-site coordination. Indeed, the frequency of particular Raman modes involving vibrations of mainly one type of atom is determined to a great extent by the interaction of these atoms with their nearest neighbors and to a lesser extent by the next-nearest-neighbor interactions. Comparison of temperature-dependent X-ray and Raman data leads to the conclusion that, although upon dehydration the SOMS structure as a whole rearranges, the basic elements of the structure—the NbO_6 octahedra and the Na-centered polyhedra—remain practically unchanged. The marked increase of the Raman line widths above 300 °C indicates the loss of long-range order.

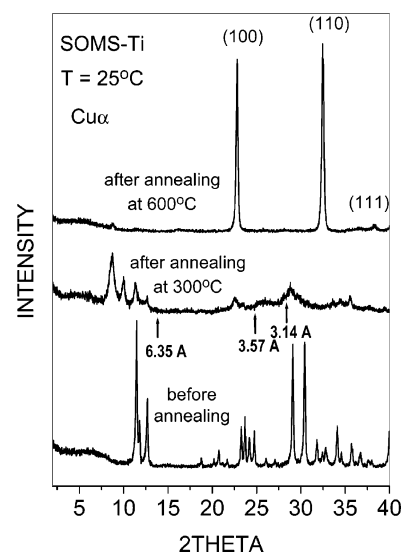


Figure 5. X-ray powder diffraction of SOMS-Ti at 25 °C : (a) without annealing, (b) after annealing in air at 300 °C for 6 h, and (c) after annealing in air at 600 °C for 6 h. The arrows indicate the positions of peaks observed for the intermediate phase during annealing in vacuo.²

Annealing above 500 °C results in drastic irreversible changes of the Raman spectra (see Figure 3), although the morphology of SOMS-perovskite microcrystals is preserved, as shown by both optical and scanning electron microscopy.² The spectrum of annealed SOMS consists of three broad bands centered (at 24 °C) at 232 , 600 , and 876 cm^{-1} . Their positions roughly correspond to the main peaks in the Raman spectra of LiNbO_3 , NaNbO_3 , and KNbO_3 ,^{7,8} but for these perovskite-like compounds the Raman lines are much narrower, the spectrum profile is more complex, and the relative line intensities are different. A simpler and broader spectrum like that of annealed SOMS may be expected for a strongly disordered structure, including a case in which only the oxygen sublattice is distorted. In ordered materials, the law of the conservation of momentum means that only zone center (Γ -point) phonons are Raman-allowed. In disordered materials, however, loss of translational symmetry results in activation of all phonon modes (or all modes related to disordered sublattice). The spectral line shape of such disorder-induced Raman scattering qualitatively reflects the smeared phonon density-of-states versus phonon energy distribution for the perfect crystal.^{9,10} Comparison of the results from the X-ray and Raman studies presented here leads to the conclusion that, in the high-temperature perovskite phase, the oxygen sublattice is strongly disordered but the cation sublattice is not disordered.

4. Conclusions

The temperature-dependent Raman studies of SOMS, SOM-Ti, and SOMS-Hf provide evidence that the structure of these materials is only weakly affected by doping. Dehydration upon annealing above 200 °C has a negligible effect on the bond lengths and force constants in the basic elements of the SOMS structure (NbO_6 octahedra and Na-centered polyhedra). Further annealing above 500 °C creates a perovskite structure with a strongly disordered oxygen sublattice. This study demonstrates the effectiveness of Raman spectroscopy for structural characterization and monitoring the structural transformations in the SOMS family of compounds.

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