1428 *Inorg. Chem.* **1998,** *37,* 1428−1429

Synthesis and Structures of New Layered Ternary Manganese Tellurides: $AMnTe_2$ (A = Li, Na)

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Received October 1, 1997

The layered structures of many transition metal chalcogenides are of interest because they are known to easily accommodate various metal ions or molecules in their van der Waals gaps.[1] Most early investigations of the first-row ternary transition metal chalcogenides concentrated on sulfides and selenides, which display a rich structural variety.[2−6] Only three types of ternary manganese telluride compounds, A_2MnTe_2 (A = K, Rb, Cs), A_6MnTe_4 (A = Na, K), and $A_2Mn_3Te_4$ (A = Rb, Cs), have been reported.[3,7,8] The first has a one-dimensional structure with edge-sharing tetrahedra, the second possesses isolated $[MnTe_4]^{6-}$ tetrahedra, and the third compound has a layered structure. We have synthesized new layered compounds, $LiMnTe_2$ and $NaMnTe_2$, by direct solid state and cation exchange reactions. These new compounds have unusual polar layers.

Since the title compounds are air and moisture sensitive, experimental operations were carried out under an inert gas atmosphere. The title compounds were synthesized by the use of welded Nb tubes that were in turn sealed in an evacuated ($\sim 10^{-4}$ Torr) silica tube. Atomic absorption (AA) measurements were performed on a Varian Spectra AA 250 Plus instrument after dissolution of the title compounds in 20% (w/w) nitric acid.

Wavelength-dispersive X-ray spectrometry (WDS) analyses were performed using a Cameca SX 50 scanning electron microscope. Samples for AA and WDS measurements were gathered by selecting crystals from the reaction products. $NaMnTe_2$ was first found in a reaction intended to yield a quaternary Na−Mn−Zr−Te compound. A 0.3 g mixture of the elements Na, Mn, Zr, and Te was combined in a molar ratio of 1:2:2:3 with NaCl (NaCl:Zr = 1:1); the resulting mixture was finely ground and transferred to a Nb tube. The temperature of the reaction vessel was raised to 1000 °C over 4 days and maintained at that temperature for 21 days, then cooled at a rate of 5 °C/h to 300 °C, and finally quenched to room temperature. Orange-red platelike crystals of $NaMnTe_2$ were observed as a minor product. After the structure and composition of $NaMnTe_2$ were determined (see below), a rational synthesis was sought. Many attempts at direct synthesis instead resulted in the formation of other compounds, including Na_6MnTe_4, and the new compounds $Na_3Mn_4Te_6$ and $Na_3Mn_{4+x}Te_6$—which are presently under investigation in our laboratory. A direct route to $NaMnTe_2$ remains elusive.

In contrast, $LiMnTe_2$ can be directly synthesized from a mixture of elements: Li (0.022 g, 3.15 mmol), Mn (0.173 g, 3.15 mmol), and Te (0.804 g, 6.30 mmol) were placed in a Nb tube under an argon atmosphere. The temperature of the reaction vessel was uniformly raised to 450 °C over 10 h, maintained at 450 °C for 1 day, uniformly increased to 750 °C over 10 h, held at that temperature for 100 h, and finally cooled to room temperature at a rate of 2 °C/h. WDS analysis of selected dark red crystals of $LiMnTe_2$ showed Mn:Te = 1.12(3):2, and no other elements heavier than Na. AA analysis yielded the composition $Li_{0.97(2)}Mn_{0.98(1)}Te_2$. $LiMnTe_2$ could also be synthesized from Li_2Te, Mn, and Te. Attempts to synthesize ternary compounds other than $LiMnTe_2$ by changing stoichiometry, reaction temperatures, and reaction times resulted in the formation of $LiMnTe_2$ as the only ternary product. Any excess Li_2Te can be separated from product $LiMnTe_2$ by washing the mixture with methanol under a nitrogen atmosphere.

With $LiMnTe_2$ in hand, $NaMnTe_2$ can be synthesized via ion exchange. An equimolar mixture of $LiMnTe_2$ (0.844 g) and NaCl (0.156 g) was placed in a Nb tube that was sealed, uniformly raised to 500 °C over 36 h, maintained at 500 °C for 2 days, then uniformly increased to 750 °C over 36 h, held at that temperature for 200 h, and finally cooled to room temperature at a rate of 2.5 °C/h. Orange-red single crystals were obtained. WDS and AA analyses gave the compositions $Na_{0.96(3)}Mn_{1.04(3)}Te_2$, and $Na_{0.97(2)}Mn_{1.06(1)}Te_2$ respectively, and showed no other elements heavier than Na. The Guinier X-ray powder pattern showed the exclusive presence of $NaMnTe_2$, and Li was not detected in the AA analysis.

Crystals of $LiMnTe_2$ and $NaMnTe_2$ with respective dimensions 0.25 × 0.22 × 0.15 and 0.22 × 0.18 × 0.02 mm were mounted in glass capillaries for X-ray studies. Data were collected for each on a Siemens R3m/V diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 20 °C.[9] The crystal structure of $NaMnTe_2$ is shown in Figure 1. $LiMnTe_2$ contains the same layered structure as $NaMnTe_2$, but Li positions could not be determined. If Li^+ ions reside in the tetrahedral sites between the $[MnTe_2]^-$ layers, then $LiMnTe_2$ could be identified as a wurtzite superstructure. Many pseudobinary compounds for which single-crystal studies have not been performed have been reported to possess the wurtzite structure, including $BeSiN_2$, $CuP(S,Se)_2$, $ZnGeN_2$, $AgInS_2$, $AlGaN_2$, $CdFeS_2$, $CdMn(S,Se)_2$, $CdZn(S,Se)_2$, and $MnZnS_2$.[10] Our attempts to refine

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S0020-1669(97)01245-7 CCC: $15.00

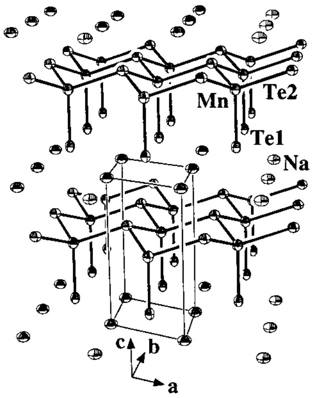

Figure 1. ORTEP plot of $NaMnTe_2$. 90% probability thermal ellipsoids are shown. Selected interatomic distances (Å) and bond angles (deg): Mn−Te1 = 2.768(5), Mn−Te2 (3×) = 2.784(2), Na−Te1 (3×) = 3.33(1), Na−Te2 (3×) = 3.21(1); Te1−Mn−Te2 = 108.9(1), Te1−Mn−Te2 = 110.04(1).

the Li positions were inconclusive. After Mn and Te atoms' locations and thermal parameters had been refined, peaks of comparable magnitude remained in both the octahedral and tetrahedral sites between the $[MnTe_2]^-$ layers. However, no convincing model emerged from attempts to locate and refine Li atoms in either or both positions.

There are two distinguishing features of the $NaMnTe_2$ structure: the asymmetry of Te binding to manganese and the intrinsic polarity of the extended structure that is thereby produced. Half of the Te atoms are bound to three manganese atoms, and half are bound to only one. Though unusual, the $NaMnTe_2$ structure can be related to a few known compounds if it is viewed as an inverse $ScCuS_2$ type.[11] The $MnTe_4$ tetrahedra are so arranged that all the Mn−Te1 vectors point in the same direction (Te1 is the terminal Te atom). In $LiMnTe_2$, the Mn−Te1 bond distance (2.786(6) Å) is slightly longer than other three Mn−Te2 bond distances (2.764(3) Å); for $NaMnTe_2$, the situation is reversed (the Mn−Te2 distance is 2.784(2) Å, and the Mn−Te1 distance is 2.768(5) Å). The $[MnTe_2]^-$ layers are held together by alkali metal cations to complete the three-dimensional structure. The Na^+ ions in $NaMnTe_2$ are in slightly irregular trigonal antiprismatic environments, having Na−Te bond distances 3 × 3.33(1) Å (Te1) and 3 × 3.21(1) Å (Te2). The shortest Te−Te contacts in $LiMnTe_2$ and $NaMnTe_2$ are 4.517(3) and 4.563(1) Å, respectively.

Magnetic susceptibility measurements were performed using selected single crystals of $LiMnTe_2$ and $NaMnTe_2$. Data were recorded with a LakeShore 7229 AC susceptometer with an external field strength of 10 Oe for $LiMnTe_2$ and a 300 series Lewis coil Faraday balance with an external field strength of 10 kOe for $NaMnTe_2$. In both cases, data were collected over the temperature range 77−298 K and were corrected for the diamagnetic contributions of the atomic cores and the sample holder. These measurements show nearly temperature-independent paramagnetism which decreases slightly from 0.006 61 emu/mol at 77 K to 0.005 54 emu/mol at 298 K for $LiMnTe_2$ and from 0.004 72 emu/mol at 77 K to 0.003 89 emu/mol at 298 K for $NaMnTe_2$. These values correspond to effective magnetic moments (μ_{eff}) less than 4.90 μ_B ($S = 2$) expected for a free Mn(III) ion in a tetrahedral field. Antiferromagnetic coupling might be responsible for the partial quenching observed, but no order−disorder transitions are apparent in the susceptibilities over this temperature range. We note that, unlike the case for systems based on tetragonal nets,[3] 3-fold symmetry of the layers should give rise to inherent frustration, and a sharp transition to a long-range spin-ordered state may be prevented.

In conclusion, we have synthesized new layered $AMnTe_2$ (A = Li, Na) compounds by solid state reactions and cation exchange techniques at 750 °C in Nb tubes. The condensation of tetrahedra into layers, $^{2}_{\infty}[\mathrm{MnTe}_{3/3}\mathrm{Te}]^-$, is of particular interest because these layers are polar and their stacking in the three dimensions preserves that polarity. Experiments underway in our laboratory include attempts to exchange the alkali metal cations for large organic counterparts that can be preferentially oriented in the polar environment of the interlaminar space.

Acknowledgment. This research was generously supported by the National Science Foundation through Grant DMR-9215890 and by the Texas Advanced Research Program through Grant 010366-097. We thank Dr. Renald Guillemette and Dr. Anatoly Bortun for their assistance with the microprobe analyses and atomic absorption measurements.

Supporting Information Available: Tables listing the details of the structure determinations, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for $LiMnTe_2$ and $NaMnTe_2$ (5 pages). Ordering information is given on any current masthead page.

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[9] (a) Crystal data for $LiMnTe_2$: space group $P3m1$ (No. 156), a = 4.517(3) Å, c = 7.187(3) Å, V = 126.99(13) Å^3, ρ_{calcd} = 4.146 g/cm^3, MW = 317.08, Z = 1, μ = 13.656 mm^{-1}. Of 833 collected reflections, 170 were unique (R_{int} = 7.54%); equivalent reflections were merged. R_1 = 5.01% and wR_2 = 9.18%. At the final stage of refinement, the difference map showed minimum and maximum peaks of −3.593 and +3.140 e/Å^3. (b) Crystal data for $NaMnTe_2$: space group $P3m1$ (No. 156), a = 4.5630(6) Å, c = 7.542(2) Å, V = 135.99(6) Å^3, ρ_{calcd} = 4.068 g/cm^3, MW = 333.13, Z = 1, μ = 12.836 mm^{-1}. Of 924 collected reflections, 232 were unique (R_{int} = 4.28%); equivalent reflections were merged. R_1 = 3.41% and wR_2 = 7.95%. At the final stage of refinement, the difference map showed minimum and maximum peaks of −1.610 and +3.261 e/Å^3.

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