

halogens too, makes reasonable to postulate decomposition in solution, $\text{Me}_2\text{bitt}^{2+}2\text{X}^- \rightarrow \text{Me}_2\text{tms} + \text{X}_2$. Although Me_2tms is characterized by one band at $277 \text{ m}\mu$,⁽⁸⁾ this is not observed in $\text{Me}_2\text{bitt}^{2+}$ solutions, perhaps because its low intensity ($\epsilon = 11,000$) as compared with the strong absorptions of $\text{Me}_2\text{bitt}^{2+}$ in that region. (b) Neglecting the well known absorptions of FeCl_4^- ,⁽⁹⁾ it seems that all bitt^{2+} compounds display two bands in the u.v. region: (i) one between 270 and $280 \text{ m}\mu$, which in the case of I_3^- derivative seems to be obscured by the strong band of I_2 at $290 \text{ m}\mu$, (ii) one more intense band near $240 \text{ m}\mu$, present in all the compounds studied, which in the case of FeCl_4^- derivative should contain the absorption of the anion too, since the intensity in $\text{Me}_2\text{bitt}^{2+}2\text{FeCl}_4^-$ is too much higher than the one reported.⁽⁹⁾ Nevertheless, no interpretation of the origin of these two bands is still available.

It is interesting to establish that $\text{Me}_2\text{bitt}^{2+}\text{CuX}_3^{2-}$ can be synthesized in two alternative ways: (a) Reaction (1), above and (b) $\text{Me}_2\text{bitt}^{2+}2\text{X}^- + \text{Cu(I)X}$ ($\text{X} = \text{Cl}, \text{Br}$). Further work is in progress about Raman spectroscopy of $\text{Me}_2\text{bitt}^{2+}$ haloderivatives, and possible reactions of type (b) with other metal halides.

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Some mixed metal tellurates

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RECENTLY Brixner [1] has reported ordered perovskites of the type $A\text{LaBWO}_6$ (where $A = \text{Sr}, \text{Ba}$; $B = \text{Li}, \text{Na}, \text{K}$). In the course of studies on the vibrational and luminescence spectra of compounds of this type in this laboratory [2] we tried to prepare the analogous tellurates.

Samples were prepared by usual techniques. Powder diffraction patterns were obtained on a Philips diffractometer using $\text{CuK}\alpha$ radiation. The spectral measurements were performed as described elsewhere [2].

We found that SrLaLiTeO_6 and BaLaLiTeO_6 are ordered perovskites with lattice parameter $a = 7.91$ and 8.04 \AA , respectively. Surprisingly enough the corresponding compounds with Y instead of La do not exist. Instead of this a.o. a garnet phase is formed with composition $\text{Y}_3\text{Li}_3\text{Te}_2\text{O}_{12}$. This compound can also be made as a single phase. Its lattice parameter amounts to 12.24 \AA .

Hexavalent uranium shows a green emission of medium intensity in the perovskites SrLaLiTeO_6 and BaLaLiTeO_6 and an intense yellow emission in the garnet $\text{Y}_3\text{Li}_3\text{Te}_2\text{O}_{12}$. This emission will be investigated further.

The vibrational spectra of these perovskite tellurates are similar to those of ordered perovskites $A_2B\text{TeO}_6$ [2]. All bands are somewhat broader than usually. This is probably due to the disorder of di- and tri-valent ions on the larger cation sites.

The vibrational spectra of the perovskites $A\text{LaBWO}_6$ differ from those of the perovskites $A_2B\text{WO}_6$ [2]. Not only are all bands broader, but also the ν_1 mode is observed in the infrared spectrum (Fig. 1). This clearly indicates a deviation from inversion symmetry which is probably due to the mixed occupation of the larger cation sites. Note that in Sr-perovskites (e.g. Sr_2MgWO_6 [3]) ν_1 is not i.r.-active. The fact that in the corresponding tellurates the ν_1 mode is not observed in the infrared spectrum may be due to spectral overlap, since the difference between the position of ν_1 (720 cm^{-1} in Raman) and ν_3 (680 cm^{-1} in i.r.) is small. The numerical values relate to SrLaLiTeO_6 .

The cation distribution in the garnet $\text{Y}_3\text{Li}_3\text{Te}_2\text{O}_{12}$ is most probably $\{\text{Y}_3\}[\text{Te}_2](\text{Li}_3)\text{O}_{12}$ in view of the preference of Te^{6+} for 6-coordination in oxides. We calculated the number of internal tellurate vibrations to be expected in the vibrational spectra assuming molecular TeO_6 groups bound together by Y^{3+} and Li^+ ions. The site symmetry of Te is S_6 , the space group $Ia3d(O_h^{10})$

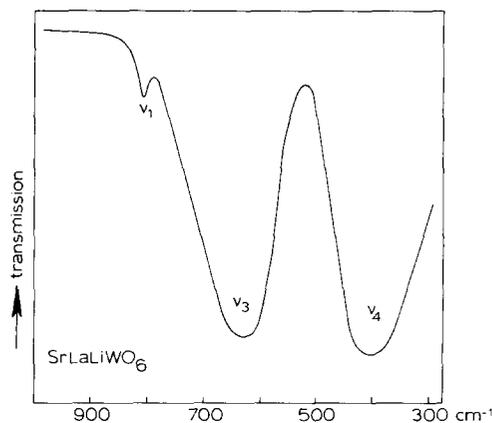


Fig. 1. I.R. spectrum of SrLaLiWO_6 in the region $900\text{--}300 \text{ cm}^{-1}$.

and there are eight Te^{6+} ions per primitive cell. As a consequence we expect two ν_1 and four ν_2 components in the Raman spectrum and three ν_3 components in the i.r. spectrum. The exclusion principle is still valid. Our experimental results are as follows (values in cm^{-1}): Raman: 750 (w, ν_1); 730 (s, ν_1); $650, 600, 530$ and 515 (all weak, ν_2); 467 and 432 (m, ν_3). i.r.: 710 (m, ν_3); 665 (s, br, ν_3); 630 (m, ν_3); 590 (s, ν_3); 490 (s, ν_4); 465 (m, ν_4); ≈ 420 (s, br, ν_4).

Our predictions are correct for the Raman spectrum; in the infrared spectrum there are more bands in the ν_3 region than expected. Perhaps there is a deviation from the ideal cation distribution. This point is under investigation.

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