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A Tellurium-125 Mössbauer Investigation of Tellurium–Tantalum and Tellurium–Niobium Oxides

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Abstract

Several compounds from the tellurium–tantalum–oxygen and tellurium–niobium–oxygen systems have been examined by ^{125}Te Mössbauer spectroscopy. The results show that tellurium(IV) occupies a distorted oxygen environment in all compounds. The ^{125}Te Mössbauer parameters also show that mixed oxides of similar compositions from different systems contain tellurium in different structural environments and, by comparison with the tellurium–vanadium–oxygen system, such features appear to reflect factors other than simple differences between the sizes of the Group VA metal ions.

Introduction

The nature of the products arising from the reaction of tellurium(IV) oxide with oxides of the Group VA elements has been the subject of recent interest. The phase diagram for the TeO_2–V_2O_5 system [1] which was determined by X-ray diffraction, revealed a new tellurium–vanadium oxide of composition $Te_2V_2O_9$ which was subsequently prepared as single crystals [2] and more recently structurally characterised by X-ray crystallography [3]. The TeO_2–Ta_2O_5 system has also been studied by X-ray diffraction [4] and four stable mixed oxides corresponding to the formulae $3TeO_2{\cdot}Ta_2O_5$, $7TeO_2{\cdot}3Ta_2O_5$ and two forms of $2TeO_2{\cdot}Ta_2O_5$ have been identified. One of the $2TeO_2{\cdot}Ta_2O_5$ modifications was later described as $TeO_2{\cdot}2Ta_2O_5$ [5] whilst $2TeO_2{\cdot}Ta_2O_5$ itself, which may also be formulated as $Te_2Ta_2O_9$, was described [4] as not being isostructural with $Te_2V_2O_9$. In a study of the TeO_2–Nb_2O_5 system [6] several mixed oxide phases described as $TeO_2{\cdot}3Nb_2O_5$, $3TeO_2{\cdot}Nb_2O_5$ and $4TeO_2{\cdot}Nb_2O_5$ have been identified. The material $3TeO_2{\cdot}Nb_2O_5$, which may also be formulated as $Te_3Nb_2O_{11}$, has been examined by single crystal X-ray crystallography [7].

X-ray diffraction has provided little evidence for any isomorphic relationship between the phases in the different oxide systems [6]. However, since all these mixed oxide phases may be considered in terms of the accomodation of tellurium(IV) in oxygen environments, it is pertinent to note that a variety of structural units have been identified in tellurium(IV)-containing oxides [8] and that ^{125}Te Mössbauer spectroscopy is well suited for the examination of the structural properties of oxides and mixed oxides containing tellurium [9–13]. We have therefore examined the phases recently identified in the tellurium–tantalum oxide and tellurium–niobium oxide systems to elucidate the nature of the coordination about tellurium in these mixed oxides.

Experimental

Samples of the tellurium–tantalum oxides and tellurium–niobium oxides were prepared from TeO_2 and either Ta_2O_5 or Nb_2O_5 as previously described [4, 6] and were supplied by Dr. J. C. J. Bart.

Tellurium-125 Mössbauer spectra were recorded with a Cryophysics microprocessor controlled Mössbauer spectrometer with both the ^{125}Sb/Rh source and the samples being maintained at 77 K. All samples contained *ca.* 10 mg ^{125}Te cm^{-2}. The drive velocity was calibrated with a ^{57}Co/Rh source and a natural iron foil. All spectra were computer fitted.

Results and Discussion

The ^{125}Te Mössbauer parameters are recorded in Table I. The chemical isomer shift data are reported relative to ^{125}I/Cu as a reference standard. A typical spectrum is depicted in Fig. 1.

The ^{125}Te Mössbauer parameters recorded from the tellurium–tantalum oxides and tellurium–

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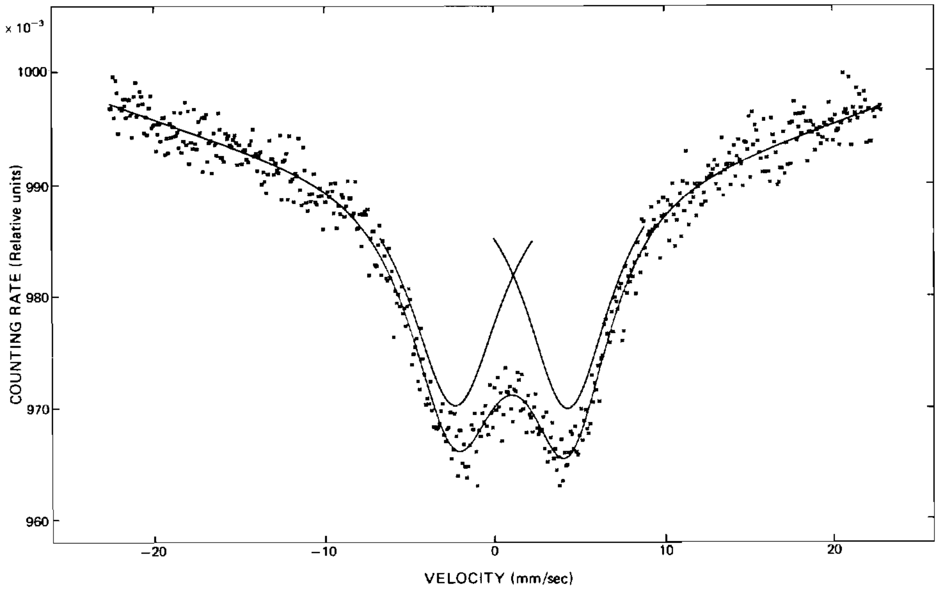


Fig. 1. ^{125}Te Mössbauer spectrum recorded from $3TeO_2{\cdot}Ta_2O_5$.

TABLE I. Tellurium-125 Mössbauer Parameters.

Compound	$\delta \pm 0.08^a$ (mm s^{-1})	$\Delta \pm 0.20$ (mm s^{-1})	Γ (mm s^{-1})
TeO_2	0.84	6.5	5.7
$3TeO_2{\cdot}Ta_2O_5$ ($Te_3Ta_2O_{11}$)	0.70	6.6	6.2
$7TeO_2{\cdot}3Ta_2O_5$ ($Te_7Ta_6O_{29}$)	0.54	6.0	5.8
$TeO_2{\cdot}2Ta_2O_5$ ($TeTa_4O_{12}$)	0.51	6.4	5.6
$4TeO_2{\cdot}Nb_2O_5$ ($Te_4Nb_2O_{13}$)	0.62	6.6	5.8
$3TeO_2{\cdot}Nb_2O_5$ ($Te_3Nb_2O_{11}$)	0.46	6.1	5.5
$TeO_2{\cdot}3Nb_2O_5$ ($TeNb_6O_{17}$)	0.53	6.0	6.2

[a] δ relative to ^{125}I/Cu.

niobium oxides are all characteristic of the presence of tellurium(IV) in oxygen environments [9–13]. In this respect it is relevant to record that several recent structural models of tellurium(IV) oxides [8, 14, 15] have involved the stereochemical activity of the lone pair of electrons on tellurium and it is therefore pertinent to note the smaller values of the ^{125}Te chemical isomer shift recorded from the compounds described here as compared with those recorded [9] from the octahedral TeX_6^{2-} (X = Cl, Br, I) species which have been discussed in terms of a $5s^2$ lone pair and 3-centre-4-electron tellurium-halogen bonds using tellurium 5p orbitals. Since $\Delta R/R$ is positive for the ^{125}Te Mössbauer transition [16] the chemical isomer shift data for the tellurium–tantalum- and tellurium–niobium oxides are consistent with the participation of tellurium 5s electrons in the bonding, as occurs in other compounds containing tellurium(IV) in oxygen coordination [11–13], and which has been estimated in tellurium(IV) oxide to involve *ca.* 10% s character in the bonding orbitals [12].

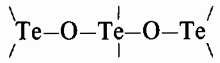
Tellurium–Tantalum Oxides

The lack of any structural information on the tellurium–tantalum oxides, all of which are formed on the tellurium-rich side of the binary system [4], precludes a rigourous interpretation of the ^{125}Te Mössbauer parameters. It is also pertinent to note the caution with which the chemical isomer shift- and quadrupole splitting-data for tellurium(IV) in oxygen environments must be interpreted since the data span only a very small range of values [9–13] and since the ^{125}Te Mössbauer parameters for a given compound, e.g. tellurium(IV) oxide, examined in different laboratories may show widespread discrepancies [10, 12, 17]. Hence any consideration of small differences in chemical isomer shift-and quadrupole splitting-data must be pursued with great care.

It is interesting however to compare the compound described [1] as $Te_9V_2O_9$, which is the only anhydrous compound isolated from the TeO_2–V_2O_5 system, with the tellurium–tantalum oxides. The description of $Te_2V_2O_9$ as a compound which is not isostructural with $Te_2Ta_2O_9$ [4] is quite reasonable given the larger size [18] of tantalum(V) in octahedral oxygen coordination (0.64 Å) as compared with that of vanadium(V) (0.54 Å). It is therefore relevant to note that the quadrupole splitting reported [13] for $Te_2V_2O_9$, Δ 6.7 mm s^{-1}, which is indicative of the degree of distortion of the electronic and lattice environment about the tellurium atom, is larger than that recorded for any of the tellurium–tantalum oxides investigated here. In this respect it is also pertinent to record that each tellurium(IV) species in $Te_2V_2O_9$ is a component of a Te_2O_5 unit and is bonded to three oxygen atoms in a pyramidal array in which the O–Te–O bond angle is greater than 90° [3]. Each tellurium atom also contains a stereochemically active lone pair of electrons which lie along the 3-fold axis thereby completing a distorted tetrahedral array about the tellurium atom [3]. The tellurium atom is accomodated in a similar environment in the compound $CuTe_2O_5$ [19] which gives a similar ^{125}Te Mössbauer quadrupole splitting Δ of 6.6 mm s^{-1} [12]. Hence the smaller quadrupole splittings recorded from the tellurium–tantalum oxides, especially those described as $7TeO_2 \cdot 3Ta_2O_5$ and $TeO_2 \cdot 2Ta_2O_5$, suggest that the environment of tellurium(IV) in these mixed oxides is more regular and/or involves a different deployment of the tellurium(IV) lone pair and perhaps implies that the tellurium adopts a site more similar to the distorted trigonal bipyramidal environment enjoyed in other oxides, e.g. tellurium(IV) oxide [20], Δ 6.5 mm s^{-1}, in which it is bonded to four oxygen atoms with the lone pair occupying the fifth position in the equatorial plane. However, the previously mentioned wide discrepancies in the ^{125}Te Mössbauer parameters reported for tellurium oxides [10, 12, 17] demand that this tentative interpretation of the quadrupole splitting data recorded from the tellurium–tantalum oxides await confirmation following the structural examination of each compound. Such caution is endorsed by the known dependence [7] of the geometry of both the TeO_3 and four-coordinated TeO_4 units in metal tellurates on the character of the metal atom, a dependence which probably emanates from the polarisability of the lone pair of electrons on tellurium. In this respect it would be especially interesting to have structural data on the compound $3TeO_2 \cdot Ta_2O_5$ which can also be formulated as $Te_3Ta_2O_{11}$, for which the ^{125}Mössbauer chemical isomer shift and quadrupole splitting are larger than in the other tellurium–tantalum oxides.

Tellurium–Niobium Oxides

The mixed oxides prepared on both the tellurium– and niobium-rich sides of the binary TeO_2–Nb_2O_5 system [6] gave ^{125}Te Mössbauer parameters (Table I) which, as a group, are not significantly different from those recorded from the tellurium–tantalum oxides.

However, it is interesting to consider the Mössbauer data recorded from the tellurium–niobium oxide described as $3TeO_2 \cdot Nb_2O_5$ [6] which corresponds to the compound $Te_3Nb_2O_{11}$ which has been examined by single crystal X-ray diffraction [7]. The structure is composed of infinite corner-sharing double Nb–O octahedra which are connected via infinite  $\diagdown\!\!/\text{Te–O–}\overset{|}{\underset{|}{\text{Te}}}\text{–O–Te}\diagup\!\!\diagdown$ strings. Each Te_3O_8 unit involves two threefold coordinated tellurium(IV) atoms in the normal pyramidal configuration whilst the fourfold coordinated tellurium(IV) has an unusual configuration in which the tellurium atom is accomodated within a tetrahedral array of oxygen atoms. The differences in coordination around the tellurium atoms in the Te_3O_8 unit cannot be distinguished from the ^{125}Te Mössbauer parameters. It is also interesting to note that although the ionic radii of tantalum(V) and niobium(V) are identical (0.64 Å) [18], tellurium–tantalum oxides of a given composition show little resemblance to tellurium–niobium oxides of the same composition [4, 6] such that $Te_3Nb_2O_{11}$ is apparently not isomorphous with $Te_3Ta_2O_{11}$, [6]. However, the infrared and Raman spectra recorded from $Te_3Ta_2O_{11}$ and $Te_3Nb_2O_{11}$ have been interpreted [6] in terms of the presence of similar structural units and in this respect it is relevant to note that the ^{125}Te Mössbauer parameters recorded from $Te_3Ta_2O_{11}$ are significantly different from those obtained from $Te_3Nb_2O_{11}$ and thereby suggest that at least the environments of the tellurium atoms in these structural units are quite different.

Given that no analogue of $Te_3Ta_2O_{11}$ or $Te_3Nb_2O_{11}$ has been found in the tellurium–vanadium–oxygen system and that a compound corresponding to $Te_2V_2O_9$ has not been identified in the tellurium–niobium oxides [6] it seems that the factors which effect the formation and the structural properties of the group VA metal tellurates(IV) are difficult to evaluate. It would appear that a full structural characterisation of the different phases is required before the Mössbauer data can be interpreted with confidence. A more rigorous appraisel of the Mössbauer parameters may necessitate an enhanced appreciation of those fundamental properties of the Group VA metals, other than the differences in ionic radii, which may influence the nature of bonding and the geometry of the tellurium–oxygen units in the mixed oxide systems.

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