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Structural peculiarities and Raman spectra of TeO_2/WO_3-based glasses: A fresh look at the problem

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ABSTRACT

Ideas currently dominating the field of structural studies of TeO_2-based glasses are critically considered. A new physically and chemically consistent approach to the constitution of binary TeO_2–WO_3 glasses is proposed, in which the reasoning coming from the Raman spectra reexamination are correlated with the basic principles of thermodynamics. Separation into two phases is suggested in such glasses. One phase is TeO_2, and another is $Te(WO_4)_2$ consisting of tetrahedral $[WO_4]^{2-}$ anions and of Te^{4+} cations. Supplementary M_nO_k oxides added to the glasses are found incorporated in the former phase, thus producing solid solutions (for M=Ti, Nb) or tellurite compounds (for M=Nd).

1. Introduction

The objective of the present work was to study the structural changes and related effects in binary TeO_2–WO_3 glasses when adding to them small amounts of modifiers Y_kO_l (Y=Ti, Nb, Nd). The compounds thus obtained were multi-component TeO_2-based glasses which generally manifest extraordinary dielectric characteristics currently regarded as very promising for nonlinear optical engineering [1]. Their nature is a challenge for the modern solid state physics and chemistry, and this is the factor determining an increasing number of the relevant investigations mainly aimed at understanding the structural particularities of those glasses (see e.g., Ref. [2]).

Very often, the key to understanding the principles of atomic arrangement and chemical constitution of the glasses are the diffraction technique or vibrational spectroscopy data on the crystalline compounds resulting from the glass crystallization [3]. Unfortunately, the latter is not the case of TeO_2–WO_3 glasses. On the one hand, none of them crystallizes in a particular lattice [4], and, on the other hand, the crystal chemistry aspects of both the initial compounds, TeO_2 and WO_3, are far from the final clarity, which makes the speculations about structural features of TeO_2–WO_3 glasses a very delicate problem.

At first glance, the above circumstances seem to be responsible for the fact that despite many years of researches and the bulk of related communications, the question of the atomic arrangement of those glasses remains the open and confused question. However, a closer examination of the present state of affairs leads us to recognize that such a situation is not somewhat intrinsic exclusively in the TeO_2–WO_3 compounds, but reflects the general state of those methodological and ideological doctrines which are presently dominant in the field of structural investigations of TeO_2-based glasses, and which, we venture the opinion, are largely fallacious.

After reading a number of relevant publications (they are legion), there is the impression that most of their authors have as peculiar notions of the complex oxide glass formation as if the thermodynamic and fundamental chemical laws are not valid for processes producing those glasses. In particular, the point that these processes would result in quite distinctive chemical compounds, namely, the oxide salts, is beyond considerations, and the complex anions necessarily representing the basic structural fragments of the salts, i.e., of the glasses under study, are never discussed and even mentioned.

Instead of this, hazy notions of certain atomic “groups” or “units” lacking any objective sense are universally used. The existence of such species is customarily asserted without any argumentation, just announcing “it is well known that ….” Their chemical nature and genesis are never considered, so that nothing straitens to proclaim extravagant ideas of their atomic structures

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and vibrational properties. The invariable and universal conclusions are that the TeO_2-based glasses do contain "TeO_3 groups" into which the initial "TeO_4 groups" of TeO_2 glass are converted. The fact that such a conversion ($TeO_4 \rightarrow TeO_3$) would lower the total number of Te–O bonds in the thermodynamic system, thus conflicting with its energy minimization principle, seems to be not embarrassing for the authors. Because of such a mode of thought, the analysis of the Raman spectra becomes a supplementary instrument serving to confirm the author's particular beliefs, thus loosing its role of primary, objective and informative source of knowledge. It is particularly remarkable that the basic data [5] on the single crystal polarized-light Raman scattering of the TeO_2 ground state structure (paratellurite α-TeO_2) are universally ignored.

Among such publications, those on the TeO_2–WO_3 glasses seem to represent the most dramatic case. The suspicions of this kind appear just after reading the term "tungstate–tellurite glasses" written in the title of Ref. [6] and since then widely used as the true definition of the glasses in question (see e.g., [7]), thus violating the elementary physical principles of their formations and the norms of chemical nomenclature. Actually, that term implies that two different chemical reactions would simultaneously occur during synthesizing a given binary TeO_2–WO_3 glass: one is producing a tellurite, and another is producing a tungstate. Spurred by this bizarre idea, the users of this term are looking for the signs of those two products in the Raman spectra of the glass, and, indeed, find them where really they are not. Well documented outlines of a general situation in this field are sketched in Ref. [7]. Although the earliest publications [8] are mainly devoid of such features, the questions of chemical and structural organization of the glasses were too cursorily examined there, and in some aspects were answered incorrectly.

Therefore, in this our paper, we wish to present some alternative, "fresh look" at that problem, based on experimental and ab initio calculation data, on detailed and clear reasoning using an objective argumentation and rigorous logic. For this aim, before discussing the proper topic of the TeO_2–WO_3 glass constitution, we find necessary to remind in Section 2 some facts and principles concerning the formation, chemical nomenclature, structural and vibrational properties of solid complex oxides in focusing our attention on the TeO_2-related glasses. There we note the main points causing the confusion in this domain. Then, the experimental Raman technique and the calculation methods are described (Section 3). Results are analyzed and discussed in Section 4. The main points of the work are summarized in Section 5, and concluding remarks are made in Section 6.

2. Fundamentals

2.1. Raman spectra

By using the physical and chemical factors determining the frequencies and intensities of the vibrational bands in the Raman spectra (see, e.g., [9,10]) the three diffrent (from the spectrochemical point of view) types of the structural organization of *ionic-covalent* solid oxides X_nO_p can be distinguished.

Type A: *the homogeneous frameworks built up exclusively from* X–O–X *bridges consisting of chemically equivalent bonds*. In this case, the middle-frequency ν^{sym}_{X-O-X} bands dominate the Raman spectra, whereas no intense lines are seen at the high-frequency domain (above 600 cm^{-1}), where very weak bands of ν^{asym}_{X-O-X} vibrations are placed. The classic example of such oxides is the TeO_3-lattice (see Fig. 1) [10].

Type B: *structures in which all the* X–O *ionic-covalent bonds form quasi-isolated* XO_n *polyhedrons (ortho-groups)*, i.e., the structure in

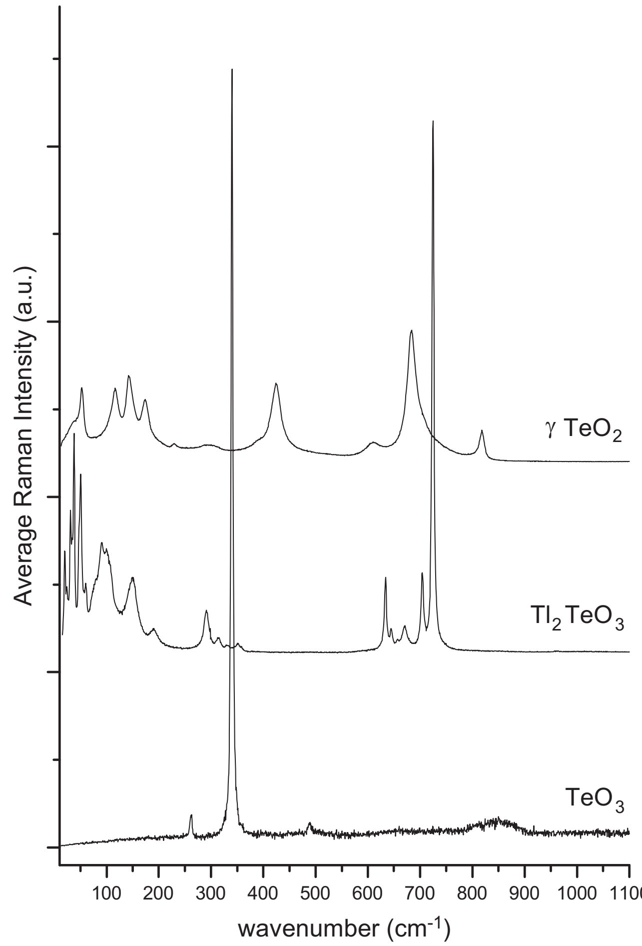

Fig. 1. Raman scattering spectra of TeO_3, Tl_2TeO_3 and γ-TeO_2 crystalline compounds.

which all those bonds are terminal. The "bridgeless" character of such compounds are displayed by their Raman spectra in which the most intense Raman active vibrations are placed in the high-frequency part (i.e., above 600 cm^{-1}), and middle-frequency region contains only weak bands. If the XO_n polyhedrons are regular, their totally symmetric ν_1 vibrations form a unique strong high-frequency band in the spectrum (see e.g., the case of Tl_2TeO_3 in Fig. 1). If the polyhedron is severely deformed, the spectrum would contain several strong bands corresponding to *individual* X–O *bond vibrations*. The case of Li_2TeO_3 [11] is a good example.

Type C**:** *structures in which the above mentioned bridges and terminal bonds are simultaneously present.* Consequently, the intense lines are seen in both the middle-frequency and high-frequency parts of the spectra. To this type, the structures in which the XO_n polyhedrons form diortho-groups, circles, chains, and layers should be attributed. It can be exemplified by the chain-type structure of γ-TeO_2 (see Fig. 1) [12].

2.2. Nomenclature, structures and Raman spectra of tellurites

By definition, the simplest tellurites (ortho-tellurites) are the salts of tellurous acid H_2TeO_3 whose $[TeO_3]^{2-}$ ortho-anions have a pyramid-like form. Theoretically, this acid can be considered as resulting from $TeO_2+H_2O=H_2TeO_3$ reaction, during which the TeO_2 molecule$\rightarrow[TeO_3]^{2-}$ *anion* conversion occurs owing to TeO_2+O^{2-} oxidation. The presence of those anions in a given complex oxide is a necessary criterion on which this oxide can be