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Origin of the strong optical nonlinearity of tellurium oxide–based compounds: The specific case of $BaTe_2O_6$

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This paper is a contribution to the understanding of the crystal chemistry origin of the strong nonlinear optical properties of tellurium oxide–based compounds. The particular case of the $BaTe_2O_6$ ($BaTe^{IV}Te^{VI}O_6$) phase has been investigated. The structure refinement using single crystal X-ray diffraction confirms that the Te^{IV} atom is located in an unclassical TeO_5 environment with one exceptionally short Te–O bond (1.82 Å) and four long ones (2.12 Å). The vibrational analysis points out that in this environment, from the spectrochemical point of view, the short bond is at the origin of a quasi-isolated $Te^{IV}O^{2+}$ molecular ion whereas the four longer bonds traduce weak interactions. Relationships have been established between the Te^{IV}–O bond lengths and the $\chi^{(3)}$ susceptibility. The four long bonds, belonging practically to the xz–plane and involving the Te^{IV} d-orbitals contribution, are at the origin of the high $\chi^{(3)}{}_{xxxx}$ and $\chi^{(3)}{}_{zzzz}$ values (30.0 and 44.3 × 10^{-13} esu respectively). The short Te–O bond, directed along the y–direction, is responsible for the lower $\chi^{(3)}{}_{yyyy}$ value (3.2 × 10^{-13} esu). This study is the first obvious confirmation for a real crystal lattice of the high superiority of the nonlinear polarizability of the weak intermolecular Te–O bonds over that of the strong molecular Te–O ones.

1. Introduction

The ‘structure-properties’ problem aims at understanding the relationships between fundamental physical characteristics of crystal lattices and the nature of their interatomic bonding. It always remains an intriguing point for the crystal chemistry and fundamental material science. The present paper focuses on the peculiarities of the atomic arrangement and the extraordinarily high nonlinear optical characteristics of tellurium oxide-based materials, more specifically in the $BaTe_2O_6$ ($BaTe^{IV}Te^{VI}O_6$) crystal lattice. From the point of view of solid state chemistry, the peculiarity of $BaTe_2O_6$ is the electronic structure of the coordination spheres of the Te^{IV} atoms, which can be at the origin of extraordinary polarization properties.

Historically, it was revealed about twenty years ago that the $\chi^{(3)}$ susceptibility for pure TeO_2 glass is about fifty times as high as that for SiO_2 [1] (and was recently confirmed for their crystalline forms as well [2,3]). This fact has aroused considerable interest in the relevant studies which initially were only slightly or not at all concerned with the question: where does this high nonlinear susceptibility come from? It was generally accepted that the Te^{IV} lone electron pairs (always present in those compounds) account for such a property [4]. However, the results of subsequent quantum chemistry *ab initio* considerations of different TeO_2 cluster models have shown that it is not the case [5–7], and the origin of those properties should be attributed to specific Te–O linkages occurring in the TeO_4 polyhedra which build up the molecular polymers or the crystal lattices of TeO_2. In every polyhedron, there are two weak linkages having length of about 2.1 Å, while the rest two (about 1.9 Å in length) form a TeO_2 molecular–like unit whose geometry is close to that of the isolated molecule. So, the last mentioned fact allows regarding the TeO_2 lattices (three polymorphs α– [8], β– [9] and γ–TeO_2 [10]) as molecular crystals in which the long linkages are intermolecular bonds. According to the *ab initio* calculation results, in which the total nonlinear polarizability values of TeO_2–made clusters were separated into intramolecular and intermolecular contributions, the weak intermolecular Te–O bonds represent the main source of the extraordinarily high $\chi^{(3)}$ susceptibility for solid forms of TeO_2.

Generally, TeO_2–based complex oxides are constituted of TeO_4 and/or TeO_{3+1} and/or TeO_3 polyhedra which depend on the nature

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and quantity of the added modifier oxide (see Fig. 1 and for example [11–15]). Very little information on the presence of Te^{IV} coordination spheres other than the above-mentioned can be found in the literature. One example was evidenced in the $Cs_2Te_4O_{12}$ (Cs_2Te^{IV}-$Te^{VI}_3O_{12}$) crystal lattice [16] in which the Te^{IV} atom is centred in a regular $Te^{IV}O_6$ octahedron formed by six Te—O bonds (2.10 Å, see Fig. 1). The vibrational spectroscopy study complemented by the lattice dynamics analysis [17] allowed to conclude that the Te^{4+} ion has no localized lone pair and, jointly with the Cs^+ ions, play the role of quasi-isolated cations, implying that this compound is a tellurate (but not tellurite) with a complex $[Te^{VI}_3O_{12}]^{6-}$ anion. Another unusual type of polyhedron is found in the $BaTe_2O_6$ ($BaTe^{IV}Te^{VI}O_6$) crystal lattice [18]: it contains a particular $Te^{IV}O_5$ symmetric tetragonal pyramid in which the Te^{IV} atom forms one exceptionally short Te—O bond (1.83 Å) in the opposite direction of the Te^{IV} lone electron pair, and four much longer equivalent Te—O bonds (2.13 Å) (Fig. 1). The longest Te—O separations can be readily specified by a mainly electrostatic attraction, the shortest bond has an essentially covalent nature and therefore can be considered as a quasi-isolated molecular-like TeO^{2+} entity, which provokes a special interest to the $BaTe_2O_6$ crystal chemistry study.

It will be shown in this paper that the peculiarities of the $BaTe_2O_6$ structure offers a possibility to clarify in direct manner the contribution of the different Te—O bond types on the nonlinear optical properties. Therefore, as a starting step of this work, the crystal structure of the $BaTe_2O_6$ compound was reinvestigated by single crystal X-ray diffraction. This study was coupled with the analysis of the vibrational spectra (Raman and infrared spectra are presented for the first time) obtained from the experiment and interpreted by using the relevant first-principles and empirical calculations.

The results obtained for the $BaTe_2O_6$ compound were interpreted from the crystal chemistry point of view in focusing our attention on the TeO^{2+} fragment situated in the TeO_5 coordination sphere around Te^{IV} atoms. These data were used to discuss the central subjects of this study: the relationships between the structural peculiarities of this coordination sphere in the $BaTe_2O_6$ phase and the linear and nonlinear optical characteristics, namely the tensors of linear and second-order nonlinear susceptibilities ($\chi^{(1)}$ and $\chi^{(3)}$, respectively) which were obtained by means of quantum chemistry *ab initio* calculations. Indeed, the calculations counterbalance the lack of experimental measurements due to the difficulty of growing large single crystals suitable for optical measurements.

The present paper is organized in the following manner. The experimental and calculation methods are exposed in part 2. The results are presented and discussed in parts 3 and 4 respectively, and concluding remarks are given in part 5.

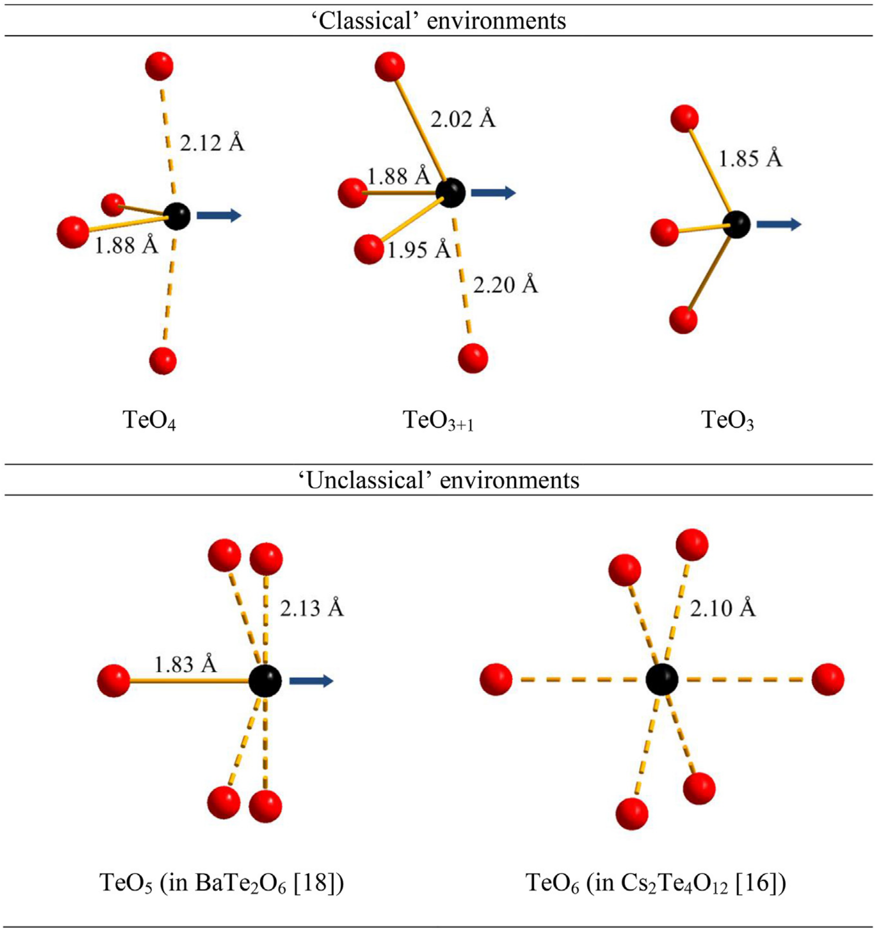

Fig. 1. Possible Te^{IV} environments in TeO_2—based materials according to the nature and quantity of the added modifier oxide. The Te core is in black, the O atoms in red and the Te lone electron pair is represented by a blue arrow. The longest Te—O bonds are represented by dashed lines. The given Te—O distance values are average values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)