Journal of Optoelectronics and Advanced Materials Vol. 2, No. 5, 2000, p. 487-492

Section 1: Single crystal materials

CRYSTAL GROWTH AND ELECTRICAL PROPERTIES OF TeO_2 SINGLE CRYSTALS

C. Neamţu, Al. Darabont[a], E. Surducan, Gh. Borodi

National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath St., P. O. Box 700, RO 3400 Cluj-Napoca 5, Romania
[b]Babeş-Bolyai University, Faculty of Physics, 1 M.Kogălniceanu St., RO 3400 Cluj-Napoca, Romania

The paper presents the preparation of the tellurium dioxide (TeO_2) compound in single crystalline state and some of its physical properties. The material is largely studied because of its piezoelectric properties and applications in acousto-optic devices. Single rystals of TeO_2 were grown by pulling from melt using the Czochralski technique in an experimental installation developed in our laboratory. The starting material was prepared in its polycrystalline state by the oxidation of metallic tellurium with concentrated azotic acid. The as resulted precipitate was dried and then thermally treated for several hours at around 400^{o}C before the growing process. The single crystals were grown at approximately 730^{o}C. The single crystalline seed crystals were obtained after repeated selections from polycrystalline boules formed during initial growing experiments. The resulted obtained single crystals were of good size and quality for subsequent measurements. The tetragonal crystalline structure reported in the literature was confirmed by X-ray diffraction measurements. The dielectrical permittivity of the single crystalline samples was determined applying the perturbation method in the X-band. The dynamics of the dielectrical properties and phase transition were studied at a frequency of 1 KHz.

Keywords: TeO_2, Tellurium dioxide, Single crystal, Czochralski, Crystal structure, Paratellurite, Dielectrical permittivity

1. Introduction

The class of Te^{IV} containing compounds, which includes tellurium dioxide (TeO_2) either in amorphous or crystalline phase, exhibits remarkable dielectric, piezoelectric, optic and electro-acoustic properties, each of them of great interest for fundamental science and technology. Potential applications of TeO_2-based glasses are directed toward optical fibre or non-linear optical devices. TeO_2 single crystals are a very promising material for use in ultrasonic generators [1] and especially in acousto-optic devices [2-4]. Such components request large single crystals with high crystalline and optical quality, high homogeneity, low light absorption and scattering and high optical power capability. Because of these specific demands, a better understanding of the growing process is very important. Recently, investigations on the growth of TeO_2 single crystals were made [5] and the effect of the growing conditions on the quality of the obtained crystals was studied [6]. The aim of this paper is to present our results regarding the growth of TeO_2 single crystals and some of its electrical properties, as a useful confirmation and extension of the above mentioned studies.

2. Experimental

2.1. Growth of TeO_2 single crystals

The polycrystalline starting material was prepared by us using the most convenient way reported in the literature [7], that is the reaction of metallic tellurium with concentrated azotic acid:

$$2\ O_2 + 2\ Te + HNO_3 \rightarrow 2\ TeO_2 \bullet HNO_3$$

After the evaporation of the solution, the as resulted [$2\ TeO_2 \bullet HNO_3$] compound was dried at 110°C. Its further heating in the 320-400°C temperature domain will determine the lose of HNO_3 and the formation of polycrystalline TeO_2.

Taking into account the following physical properties of tellurium dioxide, namely a well defined melting point, a not very significant vapour pressure at this temperature and no structural transition point between the growth and room temperature, we have concluded that TeO_2 single crystals can be obtained by pulling from the melt [8,9].

For the single crystal preparation we used the Czochralski technique. As an advantage, this method gives the possibility of obtaining quite large single crystals in relatively short periods of time.

The experimental installation developed in our laboratory is a very adaptable and easy-to-use system, allowing a fine and rapid adjustment of the necessary temperature gradient during the growth process and also of the rotation and pulling rates. While this is very useful for experiments with various materials for which one has little or no information about their behaviour during melting, the relatively short life of the incorporated electric furnace (especially at high temperatures around 1100°C) must be considered.

The polycrystalline powder was loaded in a quartz crucible of about 50 ml in volume. The temperature was constantly raised at 750°C (a little above the melting temperature, 730°C as determined by us) for 2-3 hours. After the material has melted, the melting was maintained at constant temperature for a few hours, till it turned transparent. As the seed crystal was lowered into the melt, the temperature regime was adjusted to insure the very good adherence of the melt to the seed crystal. This step is very important, because a very intimate contact between the seed and the melt is needed and this can be achieved only by a controlled partial melting of the seed crystal. After this perfect contact was obtained, the temperature was slightly reduced to allow the growth of the crystal diameter. During the growth process the crystal was rotated with 4-5 rot/min and ascended with 5 mm/h. At this stage, the growing (at constant temperature) took about 8-10 hours, after which the process was completed and the temperature of the resulted single crystal was gradually lowered to room temperature. In order to avoid the setting up of mechanical stress in the crystal, the cooling process was very slow (10-12 hours).

For the first growth processes we used a platinum wire instead of a seed crystal. In this case, the first stage represents the formation of many crystalline boules instead of a single crystal. From these boules, after several carefully controlled reductions of the growing crystal diameter, we were able to select boules with only three to six well defined single crystalline regions. In this way we chose the seed crystals we needed for subsequent growth experiments.

2.2. Crystal structure determination of TeO_2 single crystals

The first studies for an accurate determination of the crystalline structure of tellurium dioxide were made by the authors of [10, 11].

The single crystalline quality of the TeO_2 crystals obtained by us was evidenced by X-ray diffraction methods such as the Laue method, the oscillating crystal method and the Weissenberg method.

Small single crystals of approximately $0.5 \times 0.5 \times 2\ mm^3$ were cleaved from a bigger crystal of good crystalline quality. They were fixed on a goniometer head and oriented after one of the crystallographic axes with the help of the photographs obtained in the Kulpe-Schulz convergent camera (using hemicylindrical films) and the Kulpe device for the orientations correction.

The measurements were performed on a TUR M61 apparatus. The crystals were illuminated with a monochromatic beam using the Fe K_α radiation (λ = 1.9728 Å).

2.3. Electrical properties of TeO_2 single crystals

Using the microwave perturbation technique we studied the dielectrical permittivity of our TeO_2 crystalline samples. A probe having a volume of $10\ mm^3$ was mounted in a TE_{010} mode cylindrical cavity. The measurements were performed at a microwave frequency of 9.6 GHz. The complex value of the dielectrical permittivity and the loss factor of the material were determined.

The dynamics of the dielectrical properties and phase transition were studied at a frequency of 1 KHz. The experimental setup is presented in Fig. 1. The crystalline probe was fixed on a conductive sup-port connected to a Peltier element and a heat sink. The electrical contacts were made with silver paste. The temp-erature was measured using a PN-junction sen-sor. The required good thermal conductivity for the cooler-probe-thermal sensor system was ensured using silicon grease. The experimental data were collected with an ADA 2100 (USA) real time acquisition interface linked to an IBM-compatible personal computer.

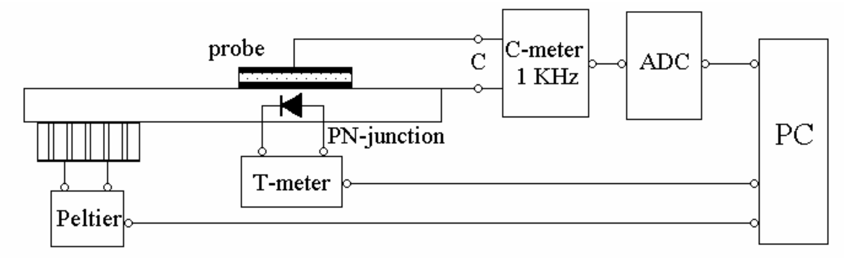

Fig. 1. Experimental setup for the study of dielectrical properties dynamics (schematic representation).

3. Results

After several growing processes and selections of adequate seed crystals (Fig. 2) we obtained TeO_2 single crystals of good crystalline quality. The bigger crystals were 50 mm long and 10 mm in diameter (Fig. 3).

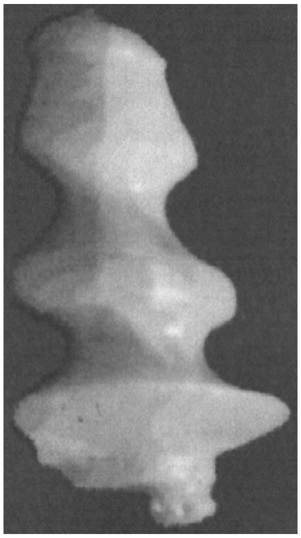

Fig. 2. Polycrystal grown on a platinum wire (its single crystalline boules were used as seed crystals for subsequent growing processes).

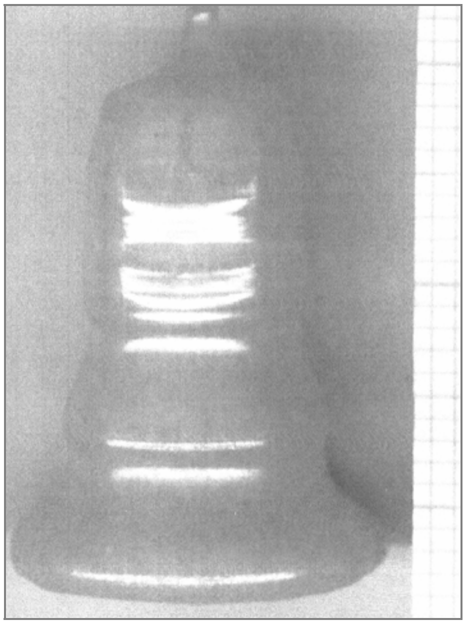

Fig. 3. TeO_2 single crystal obtained by the Czochralski method.

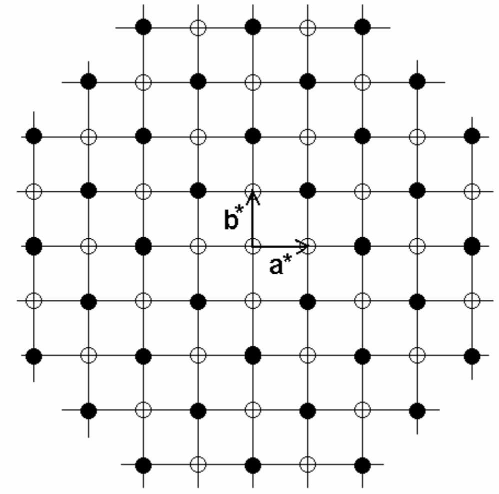

Fig. 4. Reciprocal lattice plane corres-ponding to the zero layer Weissenberg photograph when the crystal is rotated around the *c* crystallographic axis.

Regarding the crystalline structure data, from the photographs obtained by the oscillating crystal method and the Weissenberg photographs corresponding to the zero layers when the crystal is rotated around the crystallographic axes *a*, *b* and *c*, we concluded that the unit cell parameters are (as confirmed in the literature):

$$a = b = 4.81 \pm 0.05\ \text{Å}, \quad c = 7.62 \pm 0.05\ \text{Å}, \quad \alpha = \beta = \gamma = 90^{\circ}$$

giving a tetragonal symmetry.

These values were deduced from the reciprocal lattice parameters resulting from the Weissenberg photographs. Fig. 4 shows, as an example, a plane of the reciprocal lattice when the crystal is rotated around the *c* crystallographic axis.

From such a figure one can establish the systematic absences related to the lattice type and the space group determination. Thus from the above presented reciprocal lattice plane we determined that the systematic absences (or possible reflections) are $h + k = 2n + 1$, a case not mentioned in [6]. Similarly we found, using the zero layer Weissenberg photograph, that if the crystal was rotated around the *a* or *b* crystallographic axes the possible reflections were $l = 4n$ for the *00l* case and $h = 2n$ for the *h00* case (as presented in [6]).

We experimentally determined the density of the single crystalline material using the picnometer method. By mediating the results of several measurements we obtained a value of $\rho = 5{,}98$ g/cm^3. Correlating this result with the structural parameters obtained from X-ray measurements we calculated that the unit cell contains four TeO_2 molecules.

Finally using the tables given in [12], which connect the usual symmetry elements and those containing translation with the systematic absences observed in the Weissenberg photographs, we concluded that the TeO_2 crystals obtained by us have the $P4_12_12$ space group (also confirmed in the literature).

The measurements performed on our TeO_2 samples at 9.6 GHz showed that the complex value of the dielectrical permittivity is $\varepsilon = 9.43 - j0.345$. The estimated measurement errors are of 2% for the real part of the permittivity and of 5% for the imaginary one. The loss factor of the material is about 0.037.

Our experiments indicate that for lower frequencies, the dielectrical permittivity of the material is increasing. Further studies for a fixed frequency value (1 KHz) evidenced a temperature dependence of the dielectrical permittivity as presented in Fig. 5. An abrupt transition can be observed at 18-19°C.

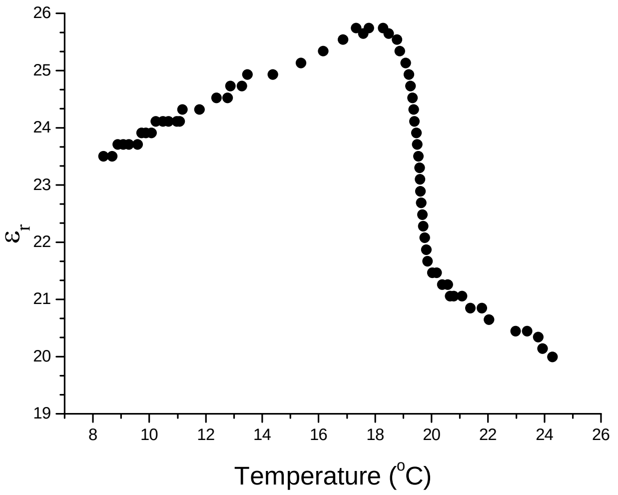

Fig. 5. Temperature dependence of the dielectrical permittivity of TeO_2 crystal (measured at 1KHz).

4. Discussion

Regarding the quality of the TeO_2 single crystals obtained by us, we can say that it was greatly influenced by the growth conditions. The initial crystals had many small cavities that were observed only after the cleaving of the crystals. The cavities were located mainly in the central part of the crystal and oriented along the pulling direction (Fig. 6).

Fig. 6. Small cavities observed in the center of a TeO_2 crystal.

The number of these cavities was substantially reduced when the crystals were repeatedly grown from the same charge of starting material by consecutive re-meltings of the previously obtained crystals. We consider that the formation of these cavities is the result of the oxygen coming out from the decomposition process of the basic material.

We have to emphasize that the quality of the crystals can be considerably improved if the pulling rate is lowered or if the crystal is grown in an oxygen atmosphere.

We also observed that the obtained crystals were less transparent in the lower part than in the top region (that is the initially growing region).

The density value of the basic material experimentally determined by us may be smaller than that determined by others because of the presence of the above mentioned cavities in the volume of the crystal.

Our results regarding the crystal structure parameters show that the TeO_2 single crystals prepared by us have the same structure, namely $P4_12_12$ space group, as described by others. This demonstrates that our crystals are paratellurite, and not another structural phase of TeO_2 [13].

The material proves to be a good dielectric (no free ions), as confirmed by the value of the loss factor we measured in the microwave X band spectrum. The structural phase transition evidenced at around 18°C was observed only for a limited number of succesive experiments. After several repeated cooling-heating cycles the structure was irreversibly modified.

5. Conclusions

Single crystals of tellurium dioxide (paratellurite) oriented along the <001> axis were grown by us using the Czochralski method. The starting material was prepared by us and the required purity was attained by subsequent growing processes. A decomposition of the initial compound was observed during the repeated melting and growing steps. This fact determined the formation of small cavities inside the crystals. The use of low pulling rates resulted in a better transparency of the crystal and the elimination of the cavities formation.

The single crystalline structure of our crystals and the crystallographic data determined by X-ray measurements confirmed the paratellurite structure and symmetry.

The crystals we obtained proved to be a good dielectric material as shown by the electrical permittivity measurements in the X-band. Further work is to be done regarding the dynamics of the dielectrical properties of TeO_2 crystals.

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