Condensed Matter Physics, 1999, Vol. 2, No. 4(20), pp. 591–594

X-ray investigations of phase transition in Bi_2TeO_5 single crystals

K.V.Domoratsky, E.F.Dudnik, V.F.Katkov, L.Ya.Sadovskaya

Dnipropetrovsk State University,
20 Kazakova Str., 320625 Dnipropetrovsk, Ukraine

Received October 12, 1998

This work is devoted to researching a phase transition in bismuth tellurite single crystals using a high-temperature X-ray analysis method. The cell parameter step-wise changes at 805 °C are revealed. Starting from the data obtained we can say that the first-type transition takes place in bismuth tellurite.

Key words: *phase transition, bismuth tellurite, X-ray, diffraction maxima*

PACS: *61.50.K*

Authors [1] consider that bismuth tellurite Bi_2TeO_5 (BTO) possesses ferroelectric properties having undergone the second-type phase transition (PT) at the temperature about 780 °C. BTO has Abm2 orthorhombic lattice a=11.602 Å, b=16.461 Å, c=5.523 Å according to [2]. The BTO single crystal belongs to the continuous solid solution group of $Bi_{1-x}Te_xO_{(3+x)/2}$ [3]. It is presumed that subcell distorted of fluorite type with the side about 5.5 Å is a basis of this solid solution structure. The unit-cell is formed by a multiplicity along cell axes 2x3x1 respectively. The temperature studies of changing cell parameters and symmetry have not been carried out earlier. Therefore the aim of this work is X-ray research of Bi_2TeO_5 single crystals in a wide temperature range including the area of phase transition supposed.

The (100), (010) and (001) single crystal plates oriented and polished with the size of 10x15x2 mm^3 and the powder of the Bi_2TeO_5 single crystals grown were used. The single crystal boules of bismuth tellurite were prepared as in the work [4] from the melt by the Czochralski technique at the starting ratio of the Bi_2O_3 and TeO_2 components 47 and 53 mole % respectively. The sample X-ray patterns were recorded with the DRON 2.0 difractometer (Co_{K_α}-radiation filtered). For the high-temperature measurements the UVD-2000 accessory was used. In table 1 the positions and the relative intensities of X-ray maxima from the BTO single crystal powder are presented at room temperature. The difractograms of BTO single crystal cuts show a=11.616 Å, b=16.451 Å and c=5.524 Å at room temperature and systematic extinctions for oriented plates taking into account non-centrosymmetry are stowed to the Abm2 space group.

Table 1. Data of X-ray maxima from the BTO single crystal powder at room temperature.

N	d, Å	I/I_0, %	hkl	N	d, Å	I/I_0, %	hkl
1	11.601	32	100	9	2.315	9	500
2	5.791	4	200	10	1.990	34	460,402
3	3.869	6	300	11	1.726	58	133
4	3.22	100	231	12	1.688	10	480
5	3.136	34	311	13	1.611	16	462
6	2.890	>100	400	14	1.108	14	971
7	2.753	14	002	15	0.910	6	176
8	2.659	4	160	16			

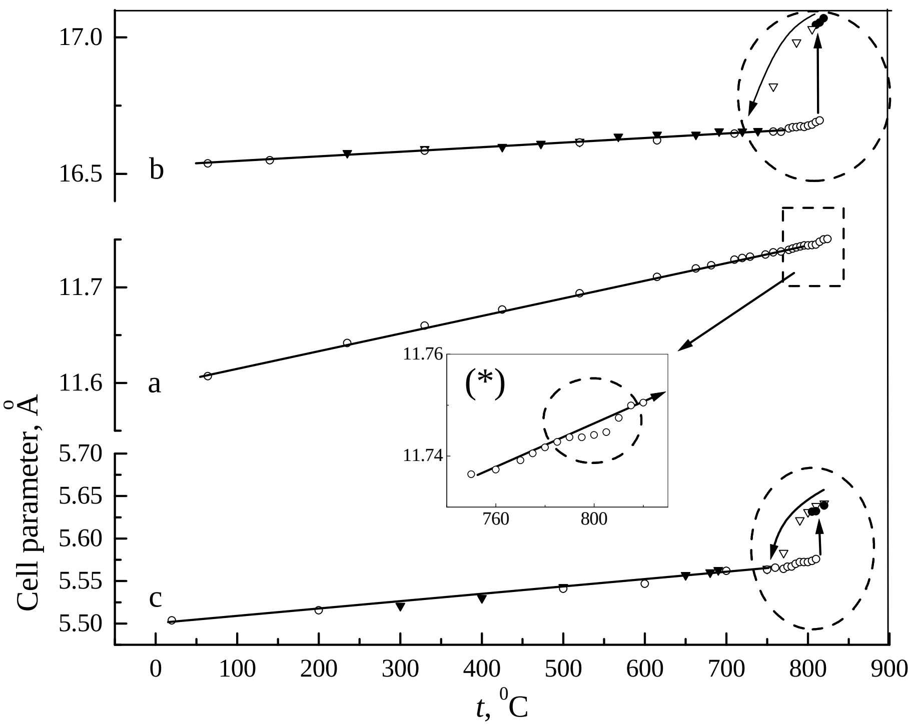

Figure 1. The temperature dependence of BTO cell parameters (changing parameters at heating are shown as circles: hollow ones are low-temperature phase, solid ones are high temperature phase; and changing at cooling are shown as downward triangles: hollow ones are high-temperature phase and solid ones are low-temperature phase).

Table 2. The most intensive maxima of the surface deposit.

N	d, Å	I/I_0, %
1	3.24	32
2	3.14	13
3	2.76	100
4	1.58	18.5
5	1.44	6.5
6	1.38	55
7	1.48	7.5
8	1.45	5

In figure 1 the temperature unit-cell parameter changes of the bismuth tellurite single crystals are showed. As it can be seen from the figure the parameters steadily increase with the temperature rise. The thermal expansion coefficients over the range of 20–780 °C are close to each other for all directions: $\alpha_a \sim 1.6 \cdot 10^{-5}$ deg^{-1} (a-axis), $\alpha_b \sim 1.2 \cdot 10^{-5}$ deg^{-1} (b-axis) and $\alpha_c \sim 1.5 \cdot 10^{-5}$ deg^{-1} (c-axis). At 805 °C parameter values increase step-wise. The largest change occurs along b-axis (Δb is $\sim$ 0.36 Å or 2.3 %). For polar axis Δc is $\sim$ 0.064 Å (1 %). The smallest step is noticed for the direction perpendicular to the cleavage surface (Δa is $\sim$ 0.006 Å or 0.05 %). The anomalies observed suggest that at 805 °C the phase transition takes place in the solid phase (melt point $\sim$ 900 °C [5]). Over the range 805–810 °C the co-existence of diffraction maxima corresponding to low- and high-temperature phases (LP and HP respectively) is noticed and the fast intensity redistribution is observed. The HP parameter values are adduced in figure 1 with the LP indexes. The transition at cooling differ from the process occurring at heating by a diffusion. The LP nucleation appears at $\sim$ 750 °C. The transition to the low-temperature phase is prolonged up to 700 °C. It should be noticed that at the thermocycling both the situation of the parameter increasing step-wise at heating and the phase transition shift and diffusion at cooling is reproduced. The character of the cell parameter change enables us to consider the first-type phase transition taking place in BTO at 805 °C. This PT temperature is somewhat higher than it is given in the work [1]. Probably that is caused by somewhat different starting component contents in the samples investigated.

At the durational high-temperature difractometer measurements of BTO single crystals cuts, the material sublimation effect appears. That is reflected in the X-ray patterns by the emerging of additional maxima which are revealed from the temperature of $\sim$ 750 °C and which last at cooling to room temperature. The substance formed is registered by sight as a yellowish-rose-tinted deposit. Moreover, while the work face of the specimen has a rough surface the back face adjoining the platinum dish practically stays undamaged. The values of the interfacial distances and relative intensities of the most intensive maxima are presented in table 2.

All these lines can hardly be connected with the onset of some single composition of the Bi_2O_3-TeO_2 system. This fact allows us to consider the surface as the coating multiphasity. As can be seen from table 2, two most intensive maxima, judging from the d multiplicity, can be referred to the same composition. At cleaning the surface coating by lapping, these maxima disappear. The chemical features of the bismuth tellurite behaviour somewhat hamper the phase transition observing. However the effects observed in figure 1 can only be explained by the structure changes, which result from the 1-st type phase transition.

The data obtained confirm the DTA research data which demonstrate the endoeffect presence at heating in the corresponding temperature region. This also indicates to the first-type phase transition.

Thus, high-temperature X-ray studies of the single crystal cuts confirmed the phase transition in bismuth tellurite single crystals but that is the 1-st type transition.

References

1. Stefanovich S.Yu., Sadovskaya L.Ya., Antonenko A.M. Phase transition in bismuth tellurite. // Sol. State Phys., 1991, vol. 37, No. 7, p. 2215–2217.
2. Mercurio D., Farissi M. El., Frit B., Goursat P. Etude structurale et densification d'un noveaux materiau piezoelectrique Bi_2TeO_5. // Mater. Chem. and Phys., 1983, vol. 12, No. 9, p. 467–476.
3. Mercurio D., Frit B., Harburn G., Parry B.H., Williams R.P., Tilley R.J.D. Diffraction patterns from ordered intergrowth phases in the Bi_2O_3-TeO_2 system. // Phys. Stat. Sol. (a), 1988, vol. 108, p. 111–122.
4. Domoratsky K.V., Kudzin A.Yu., Sadovskaya L.Ya., Sokolyanskii G.Ch. Doping influence on the physical properties of Bi_2TeO_5 single crystals. // Ferroelectrics, 1998, vol. 214, p. 191–197.
5. Földvary I., Peter A., Voszka R., Kappers L.A. Growth and properties of Bi_2TeO_5 single crystals. // J. Cryst. Growth, 1990, vol. 100, p. 75–77.

Рентгенівські дослідження фазового переходу у монокристалах Bi_2TeO_5

К.В.Доморацький, О.Ф.Дуднік, В.Ф.Катков, Л.Я.Садовська

Дніпропетровський державний університет,
320625 м. Дніпропетровськ, вул. Казакова, 20

Отримано 12 жовтня 1998 р.

Ця робота присвячена дослідженню фазового переходу в монокристалах телуриту вісмуту методом високотемпературного рентгеноструктурного аналізу. Виявлені стрибкоподібні зміни параметрів комірки при 805 °C. Виходячи з отриманих даних, можна казати, що у телуриті вісмуту має місце фазовий перехід 1-го роду.

Ключові слова: *фазовий перехід, телурит вісмуту, рентген, дифракційні максимуми*

PACS: *61.50.K*