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Ferroelastic transitions in β -BiNbO₄ and β -BiTaO₄. By A. W. SLEIGHT and G. A. JONES, *Central Research and Development Department,* E. I. du Pont de Nemours and Co., Wilmington, Delaware 19898, U.S.A.*

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Phase transitions have been discovered in β -BiNbO₄ and β -BiTaO₄ at temperatures of about 1005 and 725°C, respectively. High-temperature X-ray studies on BiTaO₄ indicate that the transition is triclinic-to-monoclinic and first order. The structures of BiTaO₄ and BiNbO₄ are shown to be of the LaTaO₄ type at high temperature. The higher transition temperature in BiNbO₄ is attributed to a greater ionicity of the Bi³⁺-O bonds in BiNbO₄ than in BiTaO₄.

Introduction

BiTaO₄ and BiNbO₄ are both known to be dimorphic (Aurivillius, 1951; Roth & Waring, 1963; Keve & Skapski, 1967). Their low-temperature (α) structure is of the orthorhombic stibiotantalite type. BiTaO₄ and BiNbO₄ are probably ferroelectric in this modification (Jeitschko & Sleight, 1974). There is a transition to a triclinic (β) modification for both BiTaO₄ and BiNbO₄ at high temperature. Apparently, the β -to- α transition is very sluggish and has, in fact, never been accomplished.

Experimental

BiTaO₄ and BiNbO₄ were synthesized by heating together appropriate mixtures of high purity Bi₂O₃, Nb₂O₅ and Ta₂O₅. X-ray powder patterns were obtained at 25°C with a Hägg-Guinier camera using Cu K α_1 radiation and an internal standard of high purity KCl ($a=6.2931$ Å). A Nonius high-temperature Guinier camera was used above room temperature. Cell dimensions were refined by least-squares calculations. DTA data were obtained with a Du Pont 990 thermal analyzer.

Results

BiTaO₄ prepared at 700°C and BiNbO₄ prepared at 1000°C were both found to be in the low-temperature α modification. When the preparation temperature was 1100°C for BiNbO₄ or in the range 800° to 1100°C for BiTaO₄, the β modification was observed. These results are in reasonable agreement with those of previous investigators.

A transition was indicated in both β -BiTaO₄ and β -BiNbO₄ by DTA. The transition was at 740°C on heating and 715°C on cooling for β -BiTaO₄ and at 1009°C on heating and 1002°C on cooling for β -BiNbO₄.

High-temperature X-ray experiments showed an abrupt structural transition in β -BiTaO₄ at about 740°C. The diffraction pattern of BiTaO₄ above 740°C was simpler

and could be completely accounted for on the basis of a monoclinic cell which is related to the triclinic cell of β -BiTaO₄. We refer to this new high-temperature modification as γ -BiTaO₄. Attempts to quench it to room temperature were unsuccessful. This is not surprising since the transition is apparently displacive rather than reconstructive.

The cell dimensions of β - and α -BiTaO₄ are given together with those of LaTaO₄ in Table 1. The similarity of cell dimensions between BiTaO₄ and LaTaO₄ is striking. Additional confirmation of the structure of γ -BiTaO₄ was obtained by calculating powder intensities based on the positional parameters reported for LaTaO₄ (Kurova & Aleksandrov, 1972). We conclude that γ -BiTaO₄ is isostructural with LaTaO₄ and that β -BiTaO₄ has a distorted version of the LaTaO₄ structure.

Discussion

The structure of β -BiNbO₄ has been determined (Keve & Skapski, 1967), and it has been established that β -BiNbO₄ and β -BiTaO₄ are isostructural (Aurivillius, 1951; Roth & Waring, 1963). The structure of LaTaO₄ has also been determined (Kurova & Aleksandrov, 1972). However, the great similarity between the structure of LaTaO₄ and that of β -BiTaO₄ has not been pointed out. In both structures, there are layers of the composition (TaO₄)_n parallel to the bc plane. Ta is octahedrally coordinated in these layers, and the octahedra share four corners but no edges or faces.

Polysynthetic twinning has been reported in LaTaO₄ crystals (Kurova & Aleksandrov, 1972). This type of twinning was also observed in β -BiNbO₄ crystals (Keve & Skapski, 1967), but here there was also a second type of twinning. We believe that the second type of twinning resulted from the γ -to- β transition. This is a ferroelastic (Aizu, 1969) transition of the type $2/m \overline{1}$, and the twinning results in ferroelastic domains. The abruptness and hysteresis of this transition indicate that it is first order.

The γ -to- β transitions in BiTaO₄ and BiNbO₄ would appear to be caused by the lone pair of electrons on Bi³⁺. Trivalent La is very similar in size to Bi³⁺, yet LaTaO₄

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Table 1. Cell dimensions

Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
β -BiTaO ₄ (25°C)	7.678	5.596	7.800	90.10	77.23	86.50	326.2
β -BiTaO ₄ (730°C)	7.739	5.668	7.814	90.13	76.44	87.19	332.7
γ -BiTaO ₄ (800°C)	7.681	5.627	7.749	90.00	78.55	90.00	328.2
LaTaO ₄ (25°C)	7.651	5.577	7.823	90.00	78.48	90.00	327.1

does not show a distortion to a triclinic structure. It is therefore interesting to examine the difference in the transition temperatures found for BiTaO_4 and BiNbO_4 , particularly, since Ta^{5+} and Nb^{5+} are essentially identical in size. The β -to- γ transition occurs at a significantly higher temperature in BiNbO_4 than in BiTaO_4 . Since Nb^{5+} -O bonding will be more covalent than Ta^{5+} -O bonding,* Bi-O bonding will be more ionic in BiNbO_4 than in BiTaO_4 . Thus, it appears that lone-pair distortions around a particular cation are promoted by high ionicity. This is consistent with what is known in simple binary compounds, e.g., PbO vs PbS . However, in the binary compounds, it is impossible to separate ionicity from size effects. Another good example of this trend in ternary compounds is found for Tl_2WO_4 and Tl_2MoO_4 . Univalent Tl is a lone-pair cation which presumably causes the transitions which exist near room temperature (Sleight, Bierlein & Bierstedt, 1975). The sizes of W^{6+} and Mo^{6+} are essentially identical, but Mo^{6+} -O bonding is significantly more covalent than W^{6+} -O bonding. The transition is at 38°C for Tl_2MoO_4 and at 11°C for Tl_2WO_4 . Thus, the

* It is both unnecessary and misleading to resort to common electronegativity values when considering the relative covalence of the Nb-O vs Ta-O bonds. The charge transfer (oxygen-to-metal) band for a niobate is always at significantly lower energy than for an analogous tantalate. Thus, the Nb-O bonding must be more covalent than Ta-O bonding (Phillips, 1970). The same considerations indicate that Mo-O bonds are more covalent than W-O bonds in analogous compounds.

higher transition temperature is found where the Tl^+ -O bonding is more ionic.

There is about a 1.4% decrease in volume when β - BiTaO_4 transforms to γ - BiTaO_4 . It is not uncommon to find a decrease in volume with increasing temperature at a transition. The reason for the decrease is presumably because the average interatomic distance in a polyhedron decreases as the polyhedron becomes more regular. Thus, negative ΔV 's should be particularly common for transitions caused by lone-pair cations. The polyhedron around the lone-pair cation will be more regular above the transition, and this causes a shorter average interatomic distance and consequently a smaller cell volume.

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