SYNTHESIS AND CRYSTAL STRUCTURE OF NOVEL NONSTOICHIOMETRIC SUBOXIDE SOLID SOLUTIONS, $Ti_{12-\delta}Ga_xBi_{3-x}O_{10}$

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Single crystals of new $Ti_{12-\delta}Ga_xBi_{3-x}O_{10}$ compounds (x = 1.42–1.74, δ = 0.77–0.62) were prepared at 900 °C with a Bi flux. Crystal structure analysis by X-ray diffraction (XRD) revealed that the solid solutions are isostructural with $Ti_{12-\delta}Sn_3O_{10}$ (cubic, space group *Fm-3m*).[1] The δ and x values were determined by refinement of the occupancies for the Ti2 and Ti4 sites, and Ga site, respectively (*Table 1*). The cell parameter *a* decreases from 13.5616(3) Å to 13.5402(5) Å with increasing Ga content, *x,* while the total valence electron number of $Ti_{12-\delta}Ga_xBi_{3-x}O_{10}$ was maintained at 117.1 by decreasing Ti defects, δ. Stella octangula is formed by sharing of the edges of four supertetrahedra composed of O-centered Ti tetrahedra and trigonal bipyramids (oxide part) (*Figure 1*). Another superpolyhedron is formed by sharing of the pyramidal planes of Ga/Bi-centered Ti mono-caped square antiprisms (intermetallic part). These two parts are incorporated in the structure. A polycrystalline bulk of a solid solution with x = 2.01, δ = 0.67 (a = 13.53772(13) Å) was synthesized by reaction sintering at 950 °C from the mixture of Ti, TiO_2, Bi_2O_3, and Ga_2O_3. The resistivities measured for the bulk were 2.2–2.4×10^{-5} Ωm in the temperature range from 10 K to 300 K.

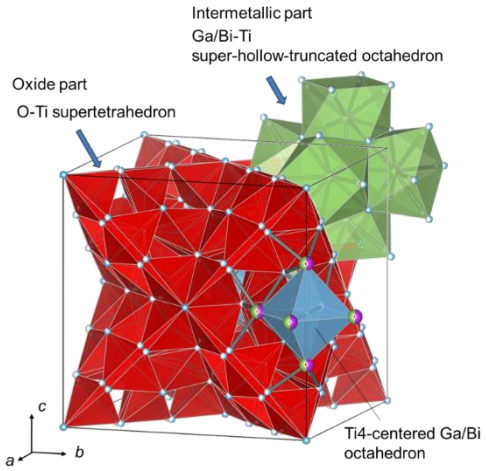

Figure 1 – Stella octangula of O-Ti supertetrahedra (oxide part) and Ga/Bi-Ti super-hollow-truncated octahedron (intermetallic part) of $Ti_{11.28}Ga_{1.51}Bi_{1.49}O_{10}$.

Table 1 Site occupancies and total number of valence electrons for $Ti_{12-\delta}Sn_3O_{10}$-type compounds.

	occupancy										
multiplicity, Wyckoff letter	96*j*	32*f*	8*c*	4*b*	4*a*		24*e*		48*g*	32*j*	total number of valence electrons per formula unit
site (valence electron number)	Ti1 (4)	Ti2 (4)	Ti3 (4)	Ti4 (4)	Ti5 (4)	Ga (3)	Sn (4)	Bi (5)	O1 (6)	O2 (6)	
$Ti_{11.31}Sn_3O_{10}$ sc. [1]	0.5	1	0.58	0.46	1	0	1	0	1	1	117.2
$Ti_{11.17}Sn_{2.45}Bi_{0.45}O_{10}$ sc.[2]	0.5	1	0.518	0.309	1	0	0.85	0.15	1	1	117.1
$Ti_{11.23}Ga_{1.42}Bi_{1.58}O_{10}$ sc.	0.5	0.818	1	0.909	1	0.472	0	0.528	1	1	117.1
$Ti_{11.27}Ga_{1.51}Bi_{1.49}O_{10}$ sc.	0.5	0.826	1	0.94	1	0.503	0	0.497	1	1	117.1
$Ti_{11.37}Ga_{1.67}Bi_{1.33}O_{10}$ sc.	0.5	0.848	1	0.953	1	0.557	0	0.443	1	1	117.1
$Ti_{11.38}Ga_{1.74}Bi_{1.26}O_{10}$ sc.	0.5	0.851	1	0.96	1	0.581	0	0.419	1	1	117.1
$Ti_{11.33}Ga_{2.01}Bi_{0.99}O_{10}$ pd	0.5	0.836	1	0.966	1	0.67	0	0.33	1	1	116.3

sc: single crystal, pd: powder

References

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