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Effect of Aluminum Content on Lattice Parameters and Unit Cell Volume in Bulk Crystals β-$(Al_xGa_{1-x})_2O_3$

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Abstract

The article studies the influence of aluminum on the lattice parameters and the unit cell volume of the binary solid solution β-$(Al_xGa_{1-x})_2O_3$. The aluminum content is determined by energy-dispersive X-ray spectroscopy. The lattice parameter values are calculated using X-ray diffractometry data. The diffraction patterns show peak broadening and shift to higher angles with increasing aluminum content. It is shown that when the aluminum fraction x changes from 0 to 0.25, the lattice parameters decrease linearly. This is consistent with Vegard's law for solid solutions. The decrease in cell volume is physically related to the fact that aluminum has a smaller ionic radius than gallium, and the Al–O bond length is shorter than Ga–O one.

Keywords: Aluminum gallium oxide; Bulk crystal; Unit cell; Lattice parameters

1. INTRODUCTION

Gallium oxide β-Ga_2O_3 is a fairly well-studied material at present in terms of both its crystal structure and electronic properties. Gallium oxide research has now shifted to the field of device applications [1]. At the same time, its binary solid solutions with other metal oxides, such as β-$(Al_xGa_{1-x})_2O_3$ or β-$(In_xGa_{1-x})_2O_3$, have been studied to a somewhat lesser extent. However, such ternary compounds allow increasing or decreasing the band gap of the material, which is the basis for engineering device heterostructures based on gallium oxide. Therefore, the effect of a substitution impurity, such as aluminum in β-$(Al_xGa_{1-x})_2O_3$, on the properties of the material (primarily on the crystal lattice) is of considerable interest.

In order to study the influence of aluminum on the properties of the lattice in the compound β-$(Al_xGa_{1-x})_2O_3$, it is necessary to determine, firstly, the preferred position that aluminum occupies in the crystal lattice, and, secondly, the lattice parameters of the oxides that make up the ternary compound, namely: Ga_2O_3 and Al_2O_3.

The monoclinic crystal structure of β-Ga_2O_3 has two nonequivalent cationic sites for the gallium ion: the tetrahedrally coordinated site (Ga1) and the octahedrally coordinated site (Ga2). Fig. 1 shows a cell of the monoclinic lattice of β-Ga_2O_3. The tetrahedral and octahedral sites of the gallium ions are shown in blue and green, respectively. The O1, O2 and O3 represent three different sites of the oxygen ions in the β-Ga_2O_3 crystal lattice.

Calculations [2,3] show that it is energetically more favorable for Al to occupy the Ga2 sites. Aluminum located in the octahedral Ga2 sites has an energy of 0.2 eV per Al atom lower than aluminum located in the tetrahedral Ga2 sites [4]. Aluminum atoms begin to occupy the Ga2 sites at sufficiently large values x of the aluminum content in the crystal. According to the data of work [5], during the

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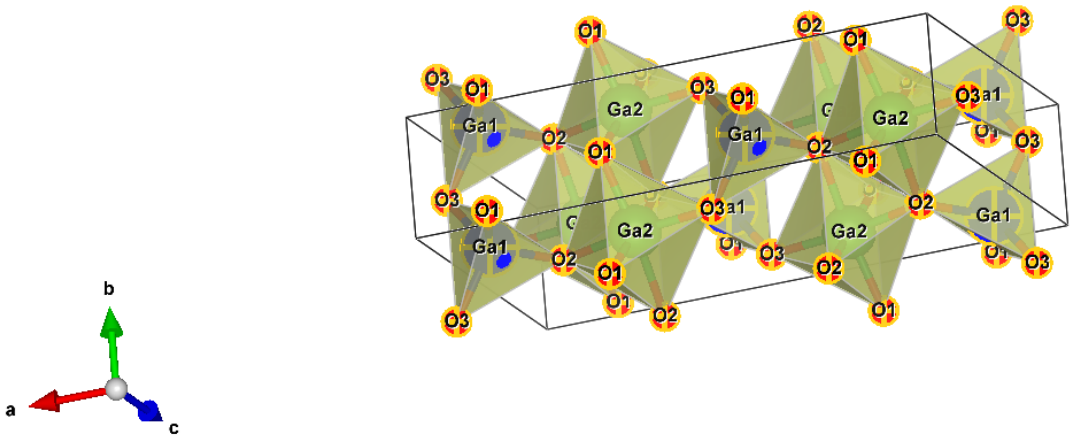

Fig. 1. Unit cell of the β-Ga_2O_3 crystal structure.

growth of bulk β-$(Al_xGa_{1-x})_2O_3$ crystals, aluminum begins to occupy the Ga1 sites at $x > 0.50$. In our case, for $x < 0.25$, we can assume that aluminum replaces gallium in the octahedral sites only.

According to the literature, the lattice parameter values of gallium oxide β-Ga_2O_3 differ among most researchers starting from the second decimal place [6]. For our studies, the lattice parameters of binary compounds were taken from database cards ICDD PDF-2 release 2014 [7]:

• β-Ga_2O_3 C2/m — 00-041-1103;
• θ-Al_2O_3 C2/m — 01-079-1559.

Note that, strictly speaking, the theta phase of aluminum oxide θ-Al_2O_3, which has the same monoclinic crystal lattice structure as β-Ga_2O_3, is stable only at temperatures below 800 °C [8]. At crystal growth temperatures of 1850 °C, only the alpha phase of aluminum oxide α-Al_2O_3 can stably exist as a substantive material. However, since during the synthesis of the binary solid solution β-$(Al_xGa_{1-x})_2O_3$, aluminum is incorporated into the sites of the monoclinic lattice of β-Ga_2O_3, the parameters of θ-Al_2O_3, which has a similar structure, are used for comparison.

2. EXPERIMENTS

In this work three samples were studied: pure gallium oxide β-Ga_2O_3 ($x = 0$), β-$(Al_{0.11}Ga_{0.89})_2O_3$ ($x = 0.11$, 4.4 at.% of Al in crystal) and β-$(Al_{0.25}Ga_{0.75})_2O_3$ ($x = 0.25$, 10 at.% of Al in crystal). The processes of growing bulk crystals of β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ were carried out in the facility "Nika-3" (production of EZAN, Russia), designed for crystal growth from the melt by the Czochralski method. The procedure for growing bulk crystals is described in more detail in Refs. [9,10].

To analyze the influence of aluminum on the lattice parameters and the unit cell volume of β-$(Al_xGa_{1-x})_2O_3$, the X-ray diffraction curves (shown in Fig. 2) were obtained from powders ground in an agate mortar on a D2Phaser powder X-ray diffractometer (Bruker AXS, Germany). Diffractometer equipped with a copper X-ray tube with a nickel β-filter ($CuK_{\alpha1\alpha2}$-radiation), a LYNXEYE semiconductor linear position-sensitive X-ray detector (Bruker AXS, Germany) with an opening of 5 angular degrees, and a vertical θ–θ goniometer with Bragg–Brentano focusing. The curves were recorded in the range of angles of 10–120 angular degrees on the 2θ scale, the registration step was 0.02 degrees, the exposure time at a point was 15 seconds.

The phase composition of the powders was determined using the specialized EVA software package (Bruker AXS, Germany) based on the ICDD PDF-2 diffraction database, release 2014 [7]. The calculation of the unit cell parameters of β-Ga_2O_3 and the determination of the features of the crystal structure of the samples were carried out by the Rietveld method with the Topas 5 software package (Bruker AXS, Germany). To eliminate random errors in determining the position of diffraction maxima, an internal NaCl standard verified with Si640f powder silicon (NIST, Gaithersburg, MD, USA) was used.

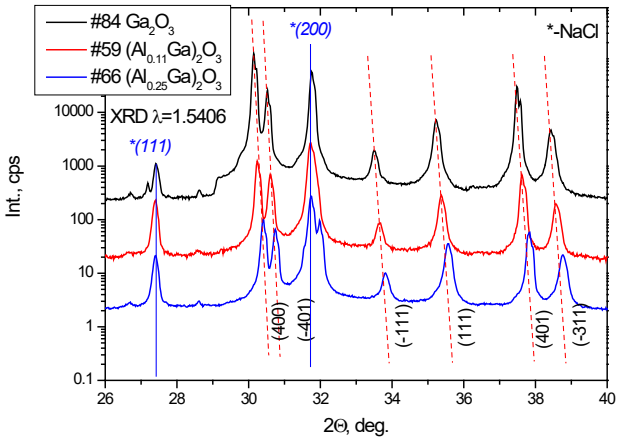

Fig. 2. 2θ-scans X-ray diffraction of β-$(Al_xGa_{1-x})_2O_3$ samples with different aluminum content x.

Table 1. Calculation data for lattice parameters and unit cell volume.

Sample	*a*, Å	*b*, Å	*c*, Å	Volume, Å^3	Al content, at.% (EDS)	Al content, *x* (EDS)
β-Ga_2O_3 (C2/m – 00-041-1103)	12.227	3.039	5.808	209.55	0	0
84, β-Ga_2O_3	12.232	3.042	5.809	209.90	0	0
59, β-$(Al_{0.11}Ga_{0.89})_2O_3$	12.179	3.026	5.787	206.99	4.4	0.11
66, β-$(Al_{0.25}Ga_{0.75})_2O_3$	12.128	3.011	5.768	204.37	10.0	0.25
θ-Al_2O_3 (C2/m – 01-079-1559)	11.854	2.904	5.622	187.92	40.0	1.00

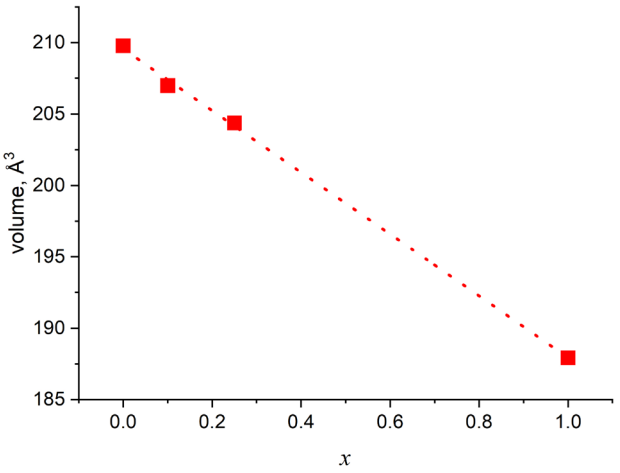

Fig. 3. Dependence of the unit cell volume on the aluminum content *x* in the β-$(Al_xGa_{1-x})_2O_3$ crystal. For reference, a tabular value of the unit cell volume for aluminum oxide ($x = 1$) has been added to the graph.

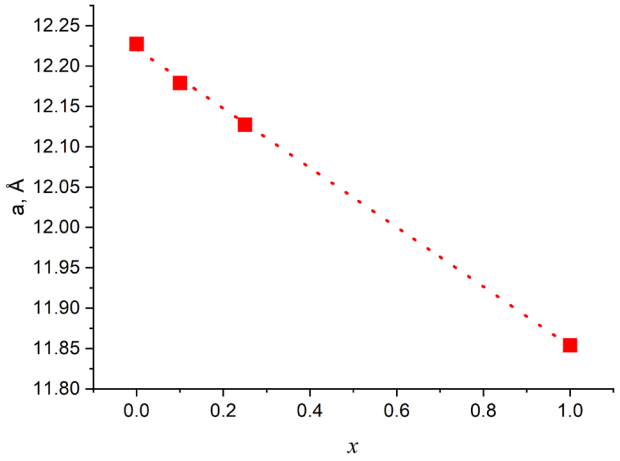

Fig. 4. Dependence of the lattice constant *a* on the content *x* of aluminum in the crystal β-$(Al_xGa_{1-x})_2O_3$.

The aluminum content in the samples was measured by energy-dispersive X-ray spectroscopy (EDS) on a Tescan MIRA-3 scanning electron microscope with an Ultim Max attachment for EDS. To check the homogeneity of the aluminum distribution over the volume of the crystal, the aluminum content was measured at five points over the surface area of each sample and then averaged. The deviation from the average value did not exceed 5% in all cases.

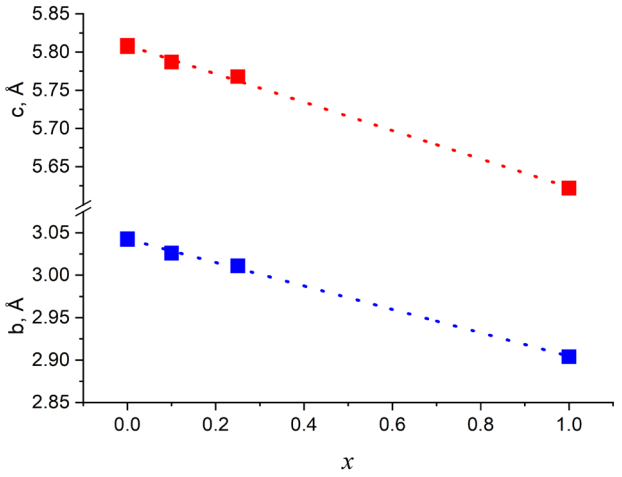

Fig. 5. Dependence of the lattice constants *b* (blue symbols) and *c* (red symbols) on the aluminum content *x* in the crystal β-$(Al_xGa_{1-x})_2O_3$.

3. RESULTS AND DISCUSSION

From Fig. 2 it can be seen that with an increase in the aluminum co ntent, the diffraction peaks shift toward larger angles θ, which indicates a decrease in the lattice parameters, and the width of the peaks increases slightly with an increase of Al, which indicates some deterioration in the crystalline quality of the material.

The obtained values of the lattice parameters (*a*, *b*, *c*) and the volume of the unit cell are given in Table 1. For reference, the tabular values of the parameters for β-Ga_2O_3 and for θ-Al_2O_3 are also given here. For clarity, the dependences of all obtained values on the aluminum content are shown graphically in Figs. 3–5. It is well seen that the lattice parameters decrease with an increase in the aluminum content according to a linear law, which is consistent with Vegard's rule.

The results of determining the average size of coherent scattering regions (CSR) and the magnitude of microstresses obtained from the profile analysis data are presented in Table 2. Here R_{wp} is the profile-weighted divergence factor of the experimental and calculated X-ray diffraction patterns. Analysis of the obtained structural data shows that the broadening of the diffraction peaks with increasing of aluminum content is associated with an increase in microstresses in the structure.

Table 2. Calculation results of microstresses.

Sample	CSR, nm	ε_0	R_{wp}
84, β-Ga_2O_3	400	$0.8 \cdot 10^{-4}$	10.5
59, β-$(Al_{0.11}Ga_{0.89})_2O_3$	400	$2.1 \cdot 10^{-4}$	10.8
66, β-$(Al_{0.25}Ga_{0.75})_2O_3$	400	$3.0 \cdot 10^{-4}$	10.4

The physical interpretation of such behavior of the material is quite clear. The ionic radii of Ga in the tetrahedral and octahedral sites are 61 and 76 pm, respectively, while for Al they are 53 and 67.5 pm, respectively, for the same sites [11]. It is obvious that the substitutional Al ion has smaller ionic radii than the Ga ion for both positions. As a result, the lattice is compressed, which is reflected in the diffraction pattern. Also, the first-principles calculation [12] shows that in β-$(Al_xGa_{1-x})_2O_3$, the average bond length for the Al–O bonds is shorter than that of the corresponding Ga–O bonds by 3.5%.

There is another significant factor that can influence the decrease in lattice parameters. As is known, bulk gallium oxide crystals growing from a melt always contain oxygen vacancies due to the limitations of the oxygen content in the atmosphere of the growth zone. Based on the calculation of the formation energy from first principles, X. Ma et al. [12] showed that in the presence of an oxygen vacancy at the site adjacent to the Al atom, the average length of the Al–O bond decreases by 1.81% compared to the length of the Ga–O bond in the same position. This leads to additional shrinkage of the lattice volume.

4. CONCLUSION

The introduction of aluminum (substitutional impurity) into bulk crystals of gallium oxide β-Ga_2O_3 and the formation of a binary solid solution β-$(Al_xGa_{1-x})_2O_3$ leads to a decrease in the lattice parameters and the volume of the unit cell linearly with respect to the fraction x of aluminum in the crystal composition, at least for x values in the range from 0 to 0.25 (from 0 to 10 at.%). This is consistent with Vegard's law for solid solutions.

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REFERENCES

[1] A.A. Petrenko, Ya.N. Kovach, D.A. Bauman, M.A. Odnoblyudov, V.E. Bougrov, A.E. Romanov, Current State of Ga_2O_3-Based Electronic and Optoelectronic Devices. Brief Review, *Rev. Adv. Mater. Technol.*, 2021, vol. 3, no. 2, pp. 1–26.

[2] H. Peelaers, J.B. Varley, J.S. Speck, C.G. Van de Walle, Structural and electronic properties of Ga_2O_3-Al_2O_3 alloys, *Appl. Phys. Lett.*, 2018, vol. 112, no. 24, art. no. 242101.

[3] J.M. Johnson, H.-L. Huang, M. Wang, S. Mu, J.B. Varley, A.F.M. Anhar Uddin Bhuiyan, Z. Feng, N.K. Kalarickal, S. Rajan, H. Zhao, C.G. Van de Walle, J. Hwang, Atomic scale investigation of aluminum incorporation, defects, and phase stability in β-$(Al_xGa_{1-x})_2O_3$ films, *APL Mater.*, 2021, vol. 9, no. 5, art. no. 051103.

[4] T.S. Wang, W. Li, C.Y. Ni, A. Janotti, Band gap and band offset of Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ alloys, *Phys. Rev. Appl.*, 2018, vol. 10, art. no. 011003.

[5] B.W. Krueger, C.S. Dandeneau, E.M. Nelson, S.T. Dunham, F.S. Ohuchi, M.A. Olmstead, Variation of band gap and lattice parameters of β–$(Al_xGa_{1-x})_2O_3$ powder produced by solution combustion synthesis, *J. Am. Ceram. Soc.*, 2016, vol. 99, no. 7, pp. 2467–2473.

[6] J.A. Spencer, A.L. Mock, A.G. Jacobs, M. Schubert, Y. Zhang, M.J. Tadjer, A review of band structure and material properties of transparent conducting and semiconducting oxides: Ga_2O_3, Al_2O_3, In_2O_3, ZnO, SnO_2, CdO, NiO, CuO, and Sc_2O_3, *Appl. Phys. Rev.*, 2022, vol. 9, no. 1, art. no. 011315.

[7] *International Centre for Diffraction Data*, Electronic resource, URL: www.icdd.org (accessed: 02.12.2024).

[8] I. Levin, D. Brandon, Metastable alumina polymorphs: crystal structures and transition sequences, *J. Am. Ceram. Soc.*, 1998, vol. 81, no. 8, pp. 1995–2012.

[9] D.A. Bauman, D.Iu. Panov, D.A. Zakgeim, V.A. Spiridonov, A.V. Kremleva, A.A. Petrenko, P.N. Brunkov, N.D. Prasolov, A.V. Nashchekin, A.M. Smirnov, M.A. Odnoblyudov, V.E. Bougrov, A.E. Romanov, High-Quality Bulk β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ Crystals: Growth and Properties, *Phys. Status Solidi A*, 2021, no. 20, art. no. 2100335.

[10] D.A. Zakgeim, D.A. Bauman, D.I. Panov, V.A. Spiridonov, A.V. Kremleva, V.M. Smirnov, M.A. Odnobludov, A.E. Romanov, V.E. Bougrov, Growing of bulk β-$(Al_xGa_{1-x})_2O_3$ crystals from the melt by Czochralski method and investigation of their structural and optical properties, *Appl. Phys. Express*, 2022, vol. 15, art. no. 025501.

[11] I. Bhaumik, M. Soharab, R. Bhatt, A. Saxena, S. Sah, A.K. Karnal, Influence of Al content on the optical band-gap enhancement and lattice structure of $(Ga_{1-x}Al_x)_2O_3$ single crystal, *Opt. Mater.*, 2020, vol. 109, art. no. 110351.

[12] X. Ma, Y. Zhang, L. Dong, R. Jia, First-principles calculations of electronic and optical properties of aluminum-doped β-Ga_2O_3 with intrinsic defects, *Results Phys.*, 2017, vol. 7, pp. 1582–1589.

УДК 548.5

Влияние содержания алюминия на параметры решётки и объём элементарной ячейки в объёмных кристаллах β-$(Al_xGa_{1-x})_2O_3$

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Аннотация. В статье исследовано влияние алюминия на параметры решётки и объём элементарной ячейки двойного твёрдого раствора β-$(Al_xGa_{1-x})_2O_3$. Содержание алюминия определено методом энергодисперсионной рентгеновской спектроскопии. Расчёт значений параметров решётки выполнен по данным рентгеновской дифрактометрии. Дифрактограммы демонстрируют уширение пиков и смещение в сторону больших углов при увеличении содержания алюминия. В работе показано, что при изменении доли *x* алюминия от 0 до 0.25 значения параметров решётки и объёма ячейки линейно убывают. Это согласуется с законом Вегарда для твёрдых растворов. Уменьшение объёма ячейки и параметров решётки физически связывается с тем, что алюминий имеет меньший ионный радиус, чем галлий, а длина связи Al–O меньше, чем длина связи Ga–O.

Ключевые слова: оксид галлия алюминия; объёмные кристаллы; элементарная ячейка; параметры решётки