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Configuration and coordination number of cation polyhedra of tungstenbronze-type-like $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions

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Abstract

We have undertaken investigations of the crystal structures and microwave dielectric properties of the $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions. The dielectric constant is affected by the volumes of cation polyhedra in which ions are located: octahedral *B*-site for Ti ion; rhombic *A*1-site mainly for *R* ions, deformed from cuboctahedron in perovskite structure; pentagonal *A*2-site for Ba ions and trigonal *C*-site for small ions. In the more precise crystal structure, the *A*1- and *A*2-sites separate into five and two independent positions, respectively. In this study, the configurations and coordination numbers of the cation polyhedra are presented. The dielectric constant is also discussed based on the volume of these polyhedra.

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Keywords: $BaTiO_3$ and titanates; Coordination number (CN); Dielectric properties; Perovskites; X-ray methods

1. Introduction

Microwave dielectric materials are used for microwave telecommunications such as mobile phones, satellite broadcasting receivers and millimeter wave telecommunications. The application of microwave materials is greatly dependent on their following three properties: (1) quality factor: *Q*, (2) dielectric constant: ε_r and (3) temperature coefficient of resonant frequency: τ_f.

We have studied the correlation between crystal structure and microwave dielectric properties in the tungstenbronze-type-like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions[1] with high ε_r which enables the miniaturization of the resonator in mobile phone. These materials were reported in 1977 by Mudroliubova[2] in a Russian patent before Kolar's 1978 paper.[3]

The crystal structure of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions is shown in Fig. 1. The crystal data are as follows: orthorhombic *Pbnm* (No. 62), $a = 12.131$ (13), $b = 22.271$ (5), $c = 7.639$ (5) Å and $Z = 2$.[1] The fundamental structure is composed of three types of large cation sites: ten *A*1 rhombic sites in 2×2 perovskite blocks, four *A*2 pentagonal sites and four trigonal sites. The pentagonal and trigonal sites are located among the perovskite blocks which are constructed by four unit cells, and the rhombic *A*1-sites are bound within the perovskite blocks. The real crystal structure of the superlattice with doubled *c*-axis is due to tilting of TiO_6 octrahedra as shown in Fig. 1b. The configurations and coordination number (CN) of the rhombic and pentagonal sites have not been clarified. The rhombic site is distorted from cuboctahedron in the perovskite structure and the pentagonal site is also distorted.

In this work, we present the configuration and the coordination numbers of rhombic and pentagonal sites in the tungstenbronze-type-like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd, Pr and La) solid solutions based on the crystal structure analysis. In this case, we selected R = Sm with composition $x = 0.7$ wherein Sm and Ba separately occupy in *A*1 and *A*2 sites, respectively, as reported previously.[1] Thus the $x = 0.7$ composition is the ideal for the determination of coordination numbers (CN). We also present the correlation between the volume of these sites and dielectric constants.

2. Experimental

The configuration and coordination numbers of each site were obtained using crystal structure data which are

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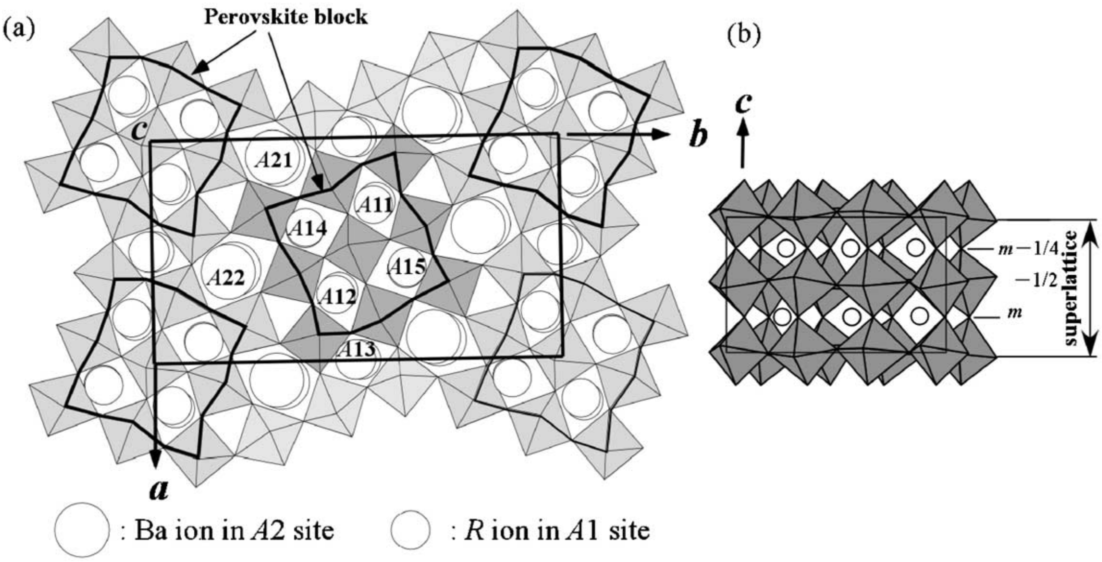

Fig. 1. Crystal structure of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solution with $x=0.7$. (a) is viewed from c-axis, (b) is viewed from perpendicular to c-axis.

refined by full-matrix least-squares refinements[4] of X-ray diffraction data[1] obtained using a single crystal difractometer. The single crystal of $R = Sm$ with $x = 0.7$ in tungstenbronze-type-like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions selected for crystal structure analysis, was grown by self-flux method.

The dielectric constants are taken from a previous report[5] which were measured by the Hakki and Coleman method.[6]

3. Results and discussion

Ideal configurations of perovskite A1-site and pentagonal A2 site in the tungstenbronze-type-like crystal structure are cuboctahedron with 12 CN and five-capped pentagonal prism with 15 CN, respectively, as shown in Fig. 2. It is clarified in this study that the former sites deform to some kind of polyhedra with 8 or 9 CN and the latter sites deform to two-cap hexahedron with 10 CN. Though there are many kinds of method for determination of CN, we determined the coordination based on the configuration of the sites and the bond lengths between cation and anions in the polyhedron as shown in Table 1 derived from coordinates[1] of the Sm-series with $x = 0.7$. When the sum of the radii of cation and anion is similar to the bond length, the bond is identified as a coordinated bond. This situation is visualized by means of the illustration of configuration with real ionic size. Fig. 3 illustrates the configuration of rhombic A1-sites and pentagonal A2-sites. Fig. 3a, b and c show a framework of TiO_6 octahedra with R and Ba ions, a framework of octahedra with oxygen ions at $z = 1/4$ or 3/4 with mirror plane on the apex of octahedron and a framework of octahedra with oxygen ions at $z = 0.5$ or 1, respectively. The effective ionic radius of O^{2-} is 1.4 Å, and those of Sm^{3+} ion in 8, 9 and 12 CN are 1.079, 1.132 and 1.24 Å, respectively, according to Shannon.[7] The determination procedure for the coordination number of the each independent polyhedron A1(1), A1(2), A1(3), A1(4) and A1(5) is shown in Fig. 4. Fig. 4a illustrates the atomic arrangements on the mirror symmetry at $z = 1/4$ around Sm with 8 CN except A1(3); some oxygen atoms make contact with the Sm ion. If we draw the oxygen with the radius of ideal 12 CN, they will overlap each other as shown in Fig. 4c; here, all oxygen ions are projected on the same level $z = 1/4$ for bond lengths of cation and oxygen having their real lengths. Moreover, Fig. 4b represents the actual Sm radius with O^{2-} ions at $z = 0$ or 1/2 levels and at $z = 1/4$, and the relationship between oxygen and Sm ions. In the case of A1(1), A1(2), A1(4) and A1(5), eight oxygen ions contact with Sm ion, so these sites are detected to be 8 CN and in the case of A1(3), 9 CN, in which case the radius of Sm ion with 9 CN is used for the illustration.

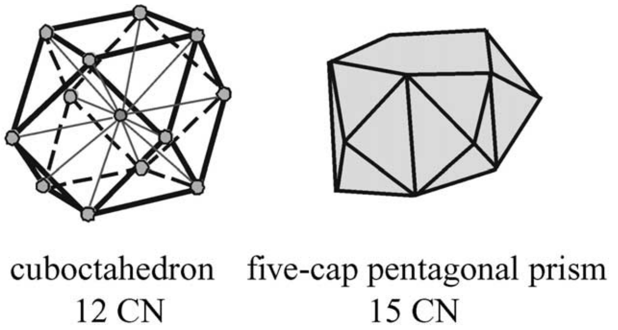
cuboctahedron 12 CN five-cap pentagonal prism 15 CN

Fig. 2. Ideal configurations of A1 and A2 sites.

On the other hand, coordinations on the pentagonal A2 sites are also determined by means of same procedure

Table 1
Bond lengths of rhombic ($A1$) and pentagonal ($A2$) polyhedra which have ideally 12 and 15 CN, respectively (bond length of real CN are shown by small solid circle)

	Bond	r/Å			Bond	r/Å	
Bond length of $A_1(1)$ site				*Bond length of $A_1(2)$ site*			
	A_1(1)–O(1)	3.0951(6)		•	A_1(2)-O(2)	2.3172(4)	
	A_1(1)–O(7)	2.9277(8)	×2		A_1(2)-O(7)	2.9993(10)	×2
•	A_1(1)–O(8)	2.4138(5)		•	A_1(2)-O(9)	2.7860(5)	
•	A_1(1)–O(10)	2.3804(9)	×2	•	A_1(2)-O(10)	2.5069(11)	×2
•	A_1(1)–O(11)	2.5602(5)		•	A_1(2)-O(11)	2.7974(7)	
•	A_1(1)–O(12)	2.5565(7)	×2		A_1(2)-O(12)	3.1303(11)	×2
•	A_1(1)–O(14)	2.6557(12)	×2	•	A_1(2)-O(14)	2.3502(8)	×2
	A_1(1)–O(17)	3.1444(7)		•	A_1(2)-O(18)	2.3203(5)	
	mean	2.6879(8)			mean	2.6829(8)	
Bond length of $A_1(3)$ site				*Bond length of $A_1(4)$ site*			
•	A_1(3)–O(7)	2.3914(9)	×2	•	A_1(4)–O(2)	2.4686(6)	
•	A_1(3)–O(7)	2.5326(11)	×2	•	A_1(4)–O(5)	2.4519(5)	
	A_1(3)–O(8)	3.1038(7)		•	A_1(4)–O(8)	2.4954(4)	
•	A_1(3)–O(9)	2.4975(5)		•	A_1(4)–O(11)	2.4569(5)	
•	A_1(3)–O(15)	2.6450(7)	×2		A_1(4)–O(12)	2.9500(12)	×2
	A_1(3)–O(15)	3.2570(11)	×2	•	A_1(4)–O(13)	2.6295(11)	×2
•	A_1(3)–O(17)	2.5262(5)			A_1(4)–O(14)	3.2567(10)	×2
•	A_1(3)–O(18)	2.4788(4)		•	A_1(4)–O(16)	2.3580(8)	×2
	mean	2.6882(8)			mean	2.6884(9)	
Bond length of $A_1(5)$ site							
•	A_1(5)–O(1)	2.4800(5)					
•	A_1(5)–O(6)	2.3393(5)					
	A_1(5)–O(9)	3.2567(6)					
	A_1(5)–O(11)	3.4890(7)					
•	A_1(5)–O(12)	2.3896(7)	×2				
•	A_1(5)–O(13)	2.4810(9)	×2				
	A_1(5)–O(14)	2.9410(7)	×2				
•	A_1(5)–O(16)	2.6108(11)	×2				
	mean	2.7008(8)					
Bond length of $A_2(1)$ site				*Bond length of $A_2(2)$ site*			
•	A_2(1)–O(1)	2.8475(6)			A_2(2)–O(2)	3.8667(9)	
•	A_2(1)–O(3)	2.8218(10)	×2	•	A_2(2)–O(3)	2.8516(9)	×2
•	A_2(1)–O(4)	2.7846(10)	×2	•	A_2(2)–O(4)	2.6632(8)	×2
•	A_2(1)–O(5)	2.7915(7)			A_2(2)–O(5)	4.0119(8)	
	A_2(1)–O(6)	3.3736(6)			A_2(2)–O(6)	3.1388(7)	
	A_2(1)–O(8)	3.6732(7)		•	A_2(2)–O(9)	3.0780(6)	
•	A_2(1)–O(13)	3.3258(9)	×2	•	A_2(2)–O(13)	2.9694(8)	×2
•	A_2(1)–O(15)	2.8255(7)	×2	•	A_2(2)–O(15)	3.0501(11)	×2
	A_2(1)–O(16)	3.5871(9)	×2		A_2(2)–O(16)	3.6600(7)	×2
	A_2(1)–O(18)	3.4122(6)		•	A_2(2)–O(17)	2.7824(5)	
	mean	3.1192(8)			mean	3.1511(8)	

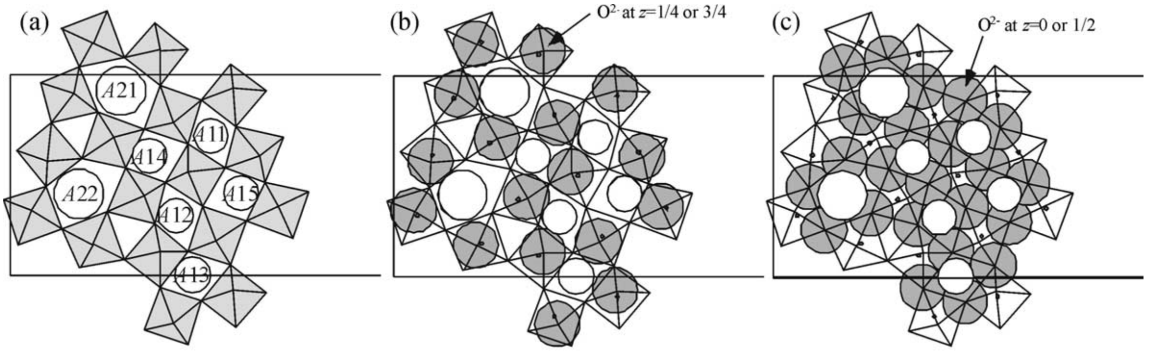

Fig. 3. Frame work (a) and arrangement of oxygen ions forming cation polyhedra. (b) shows oxygen ions surrounding cations on the $z = 1/4$ plane and (c) on the $z = 0$ or $1/2$ planes.

as described in case of the *A*1 sites. Fig. 5 shows the determination of CN of *A*2(1) and *A*2(2) sites including Ba ions with 10 CN. Ionic radii of Ba ions are 1.52 Å for 10 CN and 1.72 Å for 15 CN which was derived from Shannon's table[7] by means of extrapolation. Though the *A*2 sites are large, the Ba ions are unevenly distributed in the site and hence the CN is reduced. Two O^{2-} ions on $x=1/4$ and eight ions on $x=0$ and 1/2 are included in the CN to make the 10 coordinated polyhedra.

In Fig. 6 it is illustrated that the polyhedra of each sites is based on the coordination observed in Figs. 4 and 5. *A*1(1) and *A*1(5) sites are two-cap trigonal prisms with 8 CN, *A*1(2) and *A*1(4) sites are distorted cubic dodecahedra, and the *A*1(3) site is a three-cap trigonal prism, whereas *A*2(1) and *A*2(2) sites are two-cap hexahedra with 10 CN. The crystal structure drawn based on the new polyhedra are illustrated in Fig. 7. It is possible to see the channels along the *a*-axis, which might be the cleavage direction.

One of the dielectric properties, that is dielectric constant, is affected by the volume of cation polyhedra. Table 2 shows the dielectric constants and volumes of each cation polyhedra of the Sm series $x=0.5$ and 0.7 obtained in this study. It is clear that materials with large cation polyhedra show high dielectric properties. The dielectric constant of the solid solution with $x=0.5$ is larger than that of the solid solution with $x=0.7$. Each volume of solid solution with $x=0.5$, with high

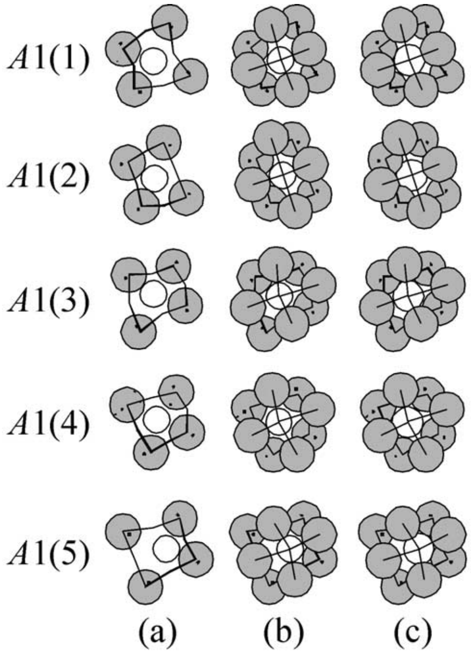

Fig. 4. Determination of coordination number of each polyhedra of rhombic *A*1 sites. (a) Oxygen ions at $z=1/4$ around Sm with 8 CN except *A*1(3) with 9 CN (b) Addition of oxygen ions at $z=0$ or 1/2 plane to (a). (c) The case of Sm with 12 CN.

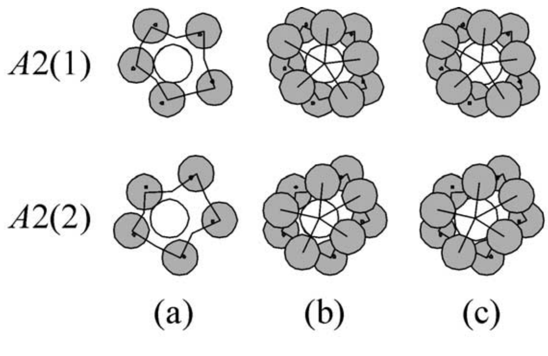

Fig. 5. Determination of coordination of each polyhedra of pentagonal *A*2 sites. (a) Oxygen ions at $z=1/4$ around Sm with 10 CN. (b) Addition of oxygen ions at $z=0$ or 1/2 plane to (a). (c) The case of Ba with 15 CN.

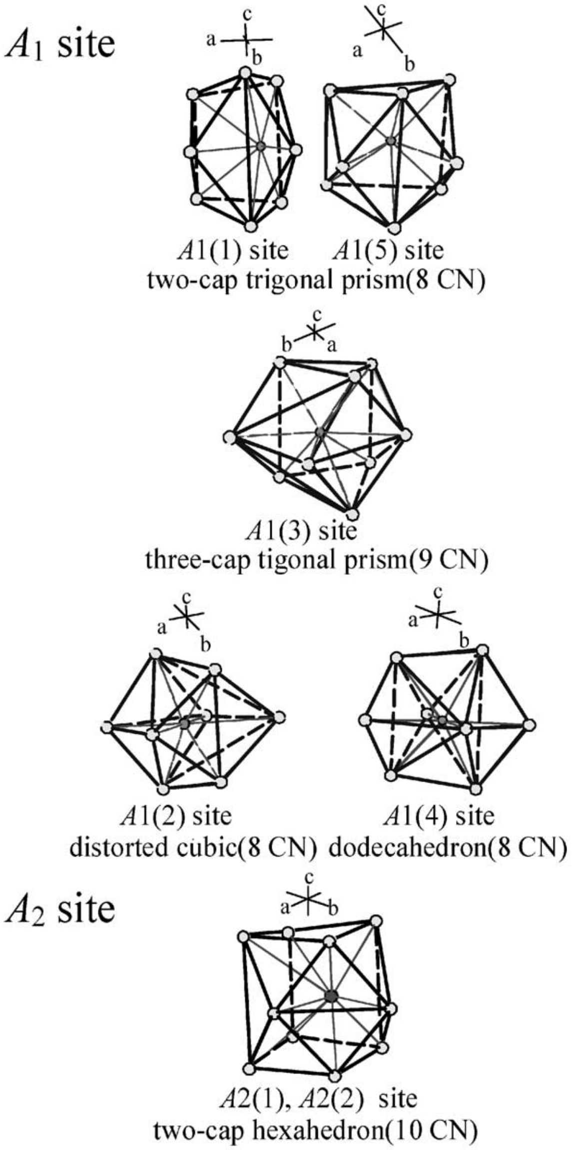

Fig. 6. Configuration of each polyhedron drawn as perspective figures.

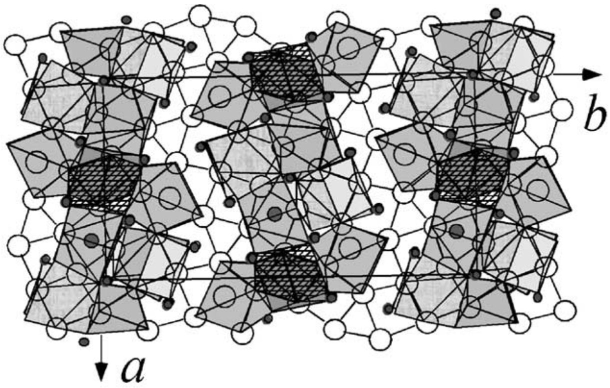

Fig. 7. Crystal structure composed of polyhedra obtained by this study.

Table 2
Dielectric constants and volume of rhombic *A*1 and pentagonal *A*2 polyhedra of tungstenbronze-type-like $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions

x	0.5	0.7
ε_r	83	79
Volume (Å³) of		
*A*1(1)	21.10	20.78
*A*1(2)	25.44	25.42
*A*1(3)	27.31	27.20
*A*1(4)	24.30	23.45
*A*1(5)	21.63	21.23
*A*2(1)	47.47	47.38
*A*2(2)	46.83	46.76

dielectric properties, is larger than that of solid solution $x=0.7$. The dielectric constant becomes larger as the volume of the polyhedron is larger.

4. Conclusion

We have determined the coordination numbers (CN) and configurations of each polyhedron in the tungstenbronze-type-like $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ crystal structure. Most of rhombic sites in the perovskite block are 8 CN, such as two-cap trigonal prisms and distorted cubic dodecahedra, and one of them is 9 CN three-cap trigonal prism. Pentagonal sites are 10 CN as two-cap hexahedra. The solid solution with large dielectric constant has large volume of polyhedra.

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References

1. Ohsato, H., Science of tungstenbronze-type-like $Ba_{6-3x}R_{8+2x}$-$Ti_{18}O_{54}$ (R = rare earth) microwave dielectric solid solutions. *J. Eur. Ceram. Soc.*, 2001, **21**, 2703–2711.
2. Mudroliubova, L. P., Rotenberg, B. A., Kartenko, N. F., Borsch, A. N., Prohvatilov, V. G., Kostikov, Yu, P. and Ivanova, M. P. *Bariumlanthanoid Tetratitanate*. USSA Certificate of Recognition 632176, 23 February 1977.
3. Kolar, D., Stadler, Z., Gaberscek, S. and Suvorov, D., Ceramic and dielectric properties of selected compositions in the BaO-TiO_2-Nd_2O_3 system. *Ber. Dt. Keram. Ges.*, 1978, **55**, 346–347.
4. Sasaki, S., A Fortran program for the least-squares refinement of crystal structures, *XL Report, ESS,* State University of New York, 1982, pp. 1–17.
5. Ohsato, H., Mizuta, M., Ikoma, T., Onogi, Z., Nishigaki, S. and Okuda, T., Microwave dielectric properties of tungsten bronze-type $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = La, Pr, Nd and Sm) solid solutions. *J. Ceram. Soc. Japan*, 1998, **106**(2), 178–182.
6. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive in the millimeter range, IRE Trans. *Microwave Theory & Tech.*, 1960, **MTT-8**, 402–410.
7. Shannon, R. D., Revised effective iomic radii and systematic studies of interatomic distance in halides and chalcogemides. *Acta Chryst.*, 1976, **A32**, 751–767.