



Article Ferroelectric Transition in Sr- and W-Doped BaTiO₃ Solid Solutions

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Abstract: We synthesized Sr- and W-doped BaTiO₃ (BTO) polycrystals by using a solid-state reaction method. The X-ray diffraction results showed that Sr and W atoms occupied the Ba and Ti sites in tetragonal BTO, respectively, and there were changes in the lattice constants and the volumes in the Sr- and W-doped BTO. We found a change in the latent heat and the Curie temperature (T_C) during the transition between the ferroelectric and paraelectric phases while increasing the contents of Sr and W in the Sr- and W-doped BTO. This can be explained by the fact that the doping of Sr and W atoms in BTO prevented a distinct transition between the ferroelectric tetragonal and paraelectric cubic structures by decreasing the c/a ratio to a value close to unity. This study shows a way toward a strategy for modulating a crystal structure by using proper dopants for future applications in ferroelectricity-based devices.

Keywords: ferroelectricity; BaTiO₃; substitution; Curie temperature

1. Introduction

In the field of condensed-matter physics, ferroelectricity has been studied for decades because spontaneous electrical polarization can be obtained without an electrostatic potential, and the direction of polarization can be tuned by using an external electric field [1–3]. Ferroelectric materials are widely applicable in piezoelectric devices, condensers, IR detectors, nonvolatile memory devices, and ferroelectric random-access memory [4–6].

Perovskite BaTiO₃ (BTO), which is the best-known ferroelectric material, undergoes a distinct transition between the ferroelectric and paraelectric phases with high latent heat (~0.3 J/g) as the transition temperature, which is called the Curie temperature (T_C) [7,8]. The ferro-paraelectric transition in BTO originates from the spontaneous transition between tetragonal and cubic structures around the T_C of 120 °C [9,10]. When the room-temperature ferroelectric phase, tetragonal BTO, is heated above T_C, the lattice constants of a and c become identical, resulting in a cubic structure, which exhibits no spontaneous polarization.

BTO has the formula of perovskite (ABO₃), and the cations Ba^{2+} and Ti^{4+} occupy the A and B sites, respectively. The dopant atoms usually have preferred substitutional sites (A or B in the perovskite ABO₃ system) depending on their atomic radius, the valence states, or their coordination numbers [11–13]. For example, Ce^{3+} atoms are more likely to occupy the A sites, while Ce^{4+} atoms are more likely to occur at the B sites [14]. Many doped BTO systems have been reported so far, and it is known that proper doping at an A or B site can effectively influence the crystal structure of BTO, as well as its ferroelectricity [15–17]. For example, A-site doping with divalent atoms, such as Sr^{2+} and Ca^{2+} , or B site-doping with tetravalent atoms, such as Zr^{4+} , Sn^{4+} , or Hf^{4+} atoms, were expected to have an effective



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). influence on ferroelectric properties, such as T_C and latent heat [18–20]. However, the effects of multivalent atoms, such as transition metal atoms, are hardly predictable for exact substitutional sites. Moreover, the ferroelectric properties can also be diverse depending on the synthetic conditions, such as temperature, ambient gas, or pressure [7].

There have been many studies of BTO systems that were doped with Sr^{2+} and that had high solubility [21]. The T_C values of Sr-doped BTO decreased with an increase in the content of Sr atoms [15]. In the case of transition metal dopants, such as tungsten (W), W dopants have possible valence states of 4+, 5+, or 6+ when tungsten atoms substitute a Ti⁴⁺ atom into a BTO system. Devi et al. reported that substitutional tungsten atoms in the hexavalent state (W⁶⁺) in BTO could effectively improve the ferroelectric properties by creating trivalent titanium (Ti³⁺) atoms due to the charge neutrality of the system [22]. Because dopants with hetero-valence states create vacancies or interstitial states, the ferroelectric properties and the phase stability of W-doped BTO are still under debate.

In this study, we showed the change in structural phase transition in polycrystalline BaTiO₃ through the doping of the A or B sites with Sr or W atoms. The Ba atoms were replaced with Sr atoms at the A sites, whereas the Ti atoms were replaced with W atoms at the B sites. X-ray diffraction revealed that the Sr- and W-doped BTO has a tetragonal structure for all samples in this study. The ratio of the lattice constants in the tetragonal structure (c/a) decreased from 1.008 to 1.005 as the content of Sr and W dopants increased. The transition between the ferroelectric tetragonal (room-temperature phase) and paraelectric cubic (high-temperature phase) structures was checked by using differential scanning calorimetry (DSC) measurements. At the transition temperature (T_C), the ferroelectricity disappeared because of the cubic structure above T_C. The values of T_C decreased while increasing the Sr content, but T_C was almost invariant with respect to the W content. The values of the latent heat during the transition gradually decreased and approached zero with the increase in the content of the Sr and W dopants. The results of this study show that the room-temperature phases of Sr-and W-doped BTO have a cube-like structure with a reduced c/a ratio; thus, the ferroelectricity of tetragonal BTO can be suppressed by doping the A and B sites in BTO.

2. Materials and Methods

BTO and BTO doped with Sr and W were synthesized by using a solid-state reaction of raw BaCO₃ (Samchun, 99.0%), TiO₂ (Sigma Aldrich, 99.8%), SrCO₃ (Sigma Aldrich, 99.9%), and WO₃ (Sigma Aldrich, 99.9%). The stoichiometric mixture was calcinated at 800 °C for 24 h and reheated at 1000 °C for 24–30 h. Intermediate fine grinding was performed between heating processes.

The differential scanning calorimetry (DSC) curves and measurements were obtained by using TA DSC 250 on a powder sample. The powder sample was put into a pan, which was then covered using a lid. An empty pan that was sealed with a lid was also used as a reference sample. The powder sample and reference sample were placed in a DSC cell. The DSC experiment was conducted in a temperature range from 25 to 184 °C with a heating rate of 10 °C/min. Then, the DSC cell was cooled to 25 °C with a cooling rate of 10 °C/min. The thermodynamic data of the powder sample were recorded during the heating and cooling processes.

The crystal structures of the BTO powders were evaluated by using X-ray diffraction (XRD, Expert pro-MPD, PANalytical) with Cu K α radiation (0.15418 nm) at the Western Seoul Center, Korea Basic Science Institute and the XRD data were analyzed by using the Rietveld refinement program of Fullprof.

The surface morphology of Sr- and W-doped BTO was studied by using a field emission scanning electron microscopy (FE-SEM) system (Hitachi SU8220 FE-SEM with a base pressure of $\sim 1 \times 10^{-8}$ Torr) at the Western Seoul Center, Korea Basic Science Institute.

3. Results and Discussion

BTO has a perovskite structure with the chemical formula of ABO₃. In this case, the Sr²⁺ atoms are located at the eight corners (A sites) of the cuboid, and the Ti⁴⁺ atoms are located at the center (B sites) of the cuboid, as seen in Figure 1a. BTO has two different phases, each of which exhibits a cubic (high-temperature phase, above the T_C) or tetragonal (room-temperature phase, below the T_C) structure. Both crystal structures are perovskite structures with different ratios between the lattice constants (c/a) (i.e., 1 for the cubic structure and >1 for the tetragonal structure). The Ti atoms are surrounded by six O²⁻ atoms, which form an octahedral shape, thereby occupying the B sites. In cubic BTO, all of the lattice constants are identical, leading to a paraelectric condition with no polarization. On the other hand, tetragonal BTO exhibits an elongation of the lattice along the c-axis. Thus, the Ti-O octahedrons have down-shifted O²⁻ atoms and up-shifted Ti⁴⁺ atoms, resulting in permanent electrical polarization. Therefore, the polarization curves of tetragonal BTO can have hysteresis curves as a function of the applied electric field (E-field), and they can retain a certain amount of polarization after removing the E-field.



Figure 1. (a) Two crystal structures of BaTiO₃; the cubic structure has a paraelectric behavior with p = 0, and the tetragonal structure has a ferroelectric behavior with $p \neq 0$. (b) X-ray diffraction patterns of the Sr- and W-doped BTO systems with tetragonal BTO as a reference (black bars). The green asterisks indicate the XRD peaks of unintentionally formed secondary phases. (c) SEM images of the Sr- and W-doped BTO systems.

The X-ray diffraction patterns of the BTO doped with Sr and W atoms are shown in Figure 1b. The BTO systems with Sr and W substitutions retained the tetragonal structure when the dopant content was x = 0.1 for Sr and y = 0.06 for W. The Sr-doped BTO had a single phase (tetragonal structure) for all values of the Sr content, but with high W content (y = 0.06). W-doped BTO has several small secondary peaks that correspond to TiO₂ and SrO [23]. This indicates that Sr atoms have a greater solubility than W atoms in the BTO

system. The SEM images revealed that the influence of Sr and W doping on the morphology and particle size was insignificant, as shown in Figure 1c.

To see the changes in the BTO lattice, we analyzed the diffraction peaks located around 32.0° and 45.0° , which corresponded to the diffractions of the (101), (110), (002), and (200) planes in tetragonal BTO. The diffraction angles of these XRD peaks (as marked with black and red bars in Figure 2a) were deduced from the Rietveld refinement results, which are summarized in Table 1. As the Sr content x increased from 0.025 to 0.1, all of the diffraction peaks of (101), (110), (002), and (200) shifted to higher diffraction angles (see Figure 2b). This indicated that the lattice constants of a and c in the Sr-doped BTO became smaller. However, with the increase in the W content y from 0.02 to 0.06, the diffraction peaks of (101), (110), (002), and (200) shifted, but the tendency of these shifts was different from that in the case of the Sr-doped BTO. With y = 0.02 and 0.04, the peaks of (101) and (002) were shifted to higher angles, while the peaks of (110) and (200) were shifted to lower angles, as seen in Figure 2c. This indicated that the lattice constant of a became larger while that of c became smaller in the case of W-doped BTO. Above y = 0.04, the diffraction angles of (101), (110), (002), and (200) were saturated without significant changes, indicating that BTO has a solubility limit for W doping at around y = 0.04. Considering the ionic radii of Ti⁴⁺ (60.5 pm) and W (66 pm, 62 pm, and 60 pm for W⁴⁺, W⁵⁺, and W⁶⁺), Ti⁴⁺ atoms might be replaced by hexavalent W^{6+} atoms because they have similar effective ionic radii [24]. However, as mentioned before, hexavalent W⁶⁺ doping creates a significant charge imbalance in the system, leading to an unstable system with considerable numbers of vacancies and interstitials. Therefore, we could also consider doping a BTO system with W⁴⁺ or W⁵⁺. The oxygen vacancies could not be expected in the BTO system doped with W^{4+} or W^{5+} for the charge compensation. Considering that the amount of oxygen was larger than the stoichiometric values in the W- and Sr-doped BTO systems (the value of $3-\delta$ was roughly 3.08 according to the EDS measurements), we could not exclude the possibility of excess oxygen in the W-doped BTO system.



Figure 2. (a) X-ray diffraction peaks of the (101), (110), (002), and (200) (b) planes of $Ba_{1-x}Sr_xTi_{1-y}WyO_{3-\delta}$ with x = 0.025, 0.05, and 0.10 and y = 0.02, 0.04, and 0.06. (c) The shifts of the XRD peaks as a function of the Sr (x) or W (y) content.

	a(Å)	c(Å)	Volume(Å ³)
BTO	3.996(5)	4.029(5)	64.36(1)
x = 0.025	3.995(5)	4.023(8)	64.23(9)
x = 0.050	3.993(2)	4.022(8)	64.14(8)
x = 0.100	3.989(4)	4.013(7)	63.88(2)
y = 0.020	3.999(1)	4.023(3)	64.34(4)
y = 0.040	4.000(8)	4.021(3)	64.36(9)
y = 0.060	4.001(1)	4.023(5)	64.41(4)

Table 1. Deduced lattice constants of $Ba_{1-x}Sr_xTi_{1-y}W_yO_{3-\delta}$.

Figure 3a shows the changes in the BTO lattice constants a and c caused by substitution with Sr and W atoms at the A and B sites. With the increase in the Sr content x, the values of the lattice constants a and b simultaneously decreased. The volume of the tetragonal structure of Sr-doped BTO also decreased from 64.36(1) to 63.88(2) Å³ (0.74%). Considering that the ionic radius of Sr²⁺ (118 pm) is smaller than that of Ba²⁺ (135 pm), the decreases in the lattice constants and the volume were reasonable. However, with the increase in the dopant content (W) in BTO, the lattice constant a increased while the lattice constant c decreased. With y = 0.06, the change in the lattice constants seemed to be saturated because a = 4.001(1) Å and c = 4.023(5) Å. The volume of W-doped BTO slightly increased with the increase in y from 64.36(1) to 64.41(4) Å³, indicating that W⁴⁺ or W⁵⁺ atoms could also be candidates as substitutional atoms at the B sites in a BTO system.



Figure 3. (a) Changes in the lattice constants (a and c) and volume (V) as functions of x and y; (b) the ratios of a and c.

In the tetragonal BTO, the lattice constants a and c had different values. We obtained the ratio of a and c to study the effects of doping at the A and B sites on the crystal structure of BTO. Initially, the BTO had a c/a ratio of 1.008, as seen in Figure 3b. The B-site doping with W atoms resulted in a c/a ratio of about 1.005–1.006, regardless of the W dopant content, while the A-site doping with Sr atoms gradually decreased the c/a ratio from 1.008 (BTO) to 1.006 (x = 0.1) as a function of x. Because the differences between a and c in the tetragonal structure became smaller, the crystal structures of the BTO doped with Sr and with W became similar to the cubic structure. This could result in an indistinct transition between the tetragonal and cubic structures in a doped BTO system with large amounts of Sr and W atoms.

To study the effects of A- and B-site doping on the transition between the tetragonal and cubic BTO structures, the DSC curves of BTO, $Ba_{1-x}Sr_xTiO_3$ (x = 0.025, 0.05, and 0.1), and $BaTi_{1-y}W_yO_3$ (y = 0.02, 0.04, and 0.06) were taken with increasing and decreasing temperatures (from room temperature to 200 °C), as seen in Figure 4a,c. With the Sr and W substitutions, the endothermic and exothermic peaks in the DSC curves were flattened and the transition ranges were broadened. The transition temperature, T_C , was obtained from the positions of the peaks in the DSC curves, and the latent heat—the enthalpy at T_C —was calculated from the integrated area of the DSC curves. The T_C of BTO was found at 123.1 °C with heating and 114.7 °C with cooling. As the Sr content x increased, the intensity of the DSC peaks around T_C decreased, and the enthalpy (marked with colors)

decreased to almost zero. With x = 0.1, the transition seemed to nearly disappear in the DSC curves. The T_C also decreased as the Sr content increased. Considering the significant decrease in the ratio of the lattice constants in the doped BTO, as mentioned above, we concluded that the substitutional Sr atoms at the A sites play a certain role in suppressing the distinct transition between the ferroelectric and paraelectric phases in BTO. This is because of the modified cube-like crystal structure, which has lattice constants (a and c) that are similar.



Figure 4. (a) The DSC curves and (b) the T_C and latent heat of $Ba_{1-x}Sr_xTiO_{3-\delta}$ with x = 0, 0.025, 0.05, and 0.1. (c) The DSC curves and (d) the T_C and latent heat of $BaTi_{1-y}W_yO_{3-\delta}$ with y = 0, 0.02, 0.04, and 0.06 when increasing or decreasing the temperature.

Figure 4c shows the DSC curves of $BaTi_{1-y}W_yO_3$ (y = 0.02, 0.04, and 0.06), which were obtained under the same experimental conditions as in the case of $Ba_{1-x}Sr_xTiO_3$. Considering the strong dependency of the Sr content on the T_C and the enthalpy in Sr-doped BTO, the T_C of the W-doped BTO seemed to be invariant with all doping contents (i.e., 123.1 °C with heating and 114.7 °C with cooling). The enthalpy of W-doped BTO gradually decreased, providing a similar change to that in the Sr-doped BTO case.

The subsequent decreases in the lattice constants in the Sr-doped BTO indicated that smaller Sr^{2+} atoms occupied the spaces that were previously occupied by larger Ba^{2+} atoms. Therefore, a significant decrease in volume was observed, together with a decrease in T_C

and the latent heat in the Sr-doped BTO. On the other hand, in the W-doped BTO, the lattice constants changed, but the volume and T_C seemed to be invariant, while the latent heat in the W-doped BTO decreased with the increase in the dopant content of W. The A-site doping with Sr atoms effectively contributed to the change in the volume of the system, which indirectly influenced the c/a ratio. However, the B-site doping with W atoms contributed to a change in the lattice constants in the tetragonal structure, which directly influenced the c/a ratio. Considering that the W atoms were located at the center of an oxygen octahedron in the W-doped BTO, the ferroelectricity originating from the off-center O^{2-} could be degraded through B-site doping by using a precisely modulated crystal field for the oxygen octahedron without changing the volume. Therefore, we insist that the doping of both the A and B sites in BTO can prevent the transition between the tetragonal and cubic structures by reducing the c/a ratio. The amount of latent heat seemed to be influenced by the c/a ratio, while the values of T_C seemed to be influenced by the volume.

4. Conclusions

Doping the A and B sites in BTO changed the lattice constants (a and c), leading to an indistinct transition between the tetragonal and cubic structures, which prevented the structural phase transition of BTO. A-site doping with Sr atoms strongly influenced the volume of the system, resulting in a decreased c/a ratio (close to unity). These universal changes in the lattice resulted in a significant decrease in T_C (down to 95 °C). On the other hand, B-site doping with W atoms did not show a significant change in volume, resulting in an invariant T_C , even though the latent heat decreased with the W content. Therefore, we found that the doping of the A and B sites in BTO could suppress the distinct transition between the tetragonal and cubic structures because of the decreased c/a ratio. Moreover, the latent heat and T_C of the doped BTO systems seemed to be influenced by their volume. The results of this study suggest a strategy the use of proper dopants for the modulation of the crystal structure for future applications in ferroelectricity-based devices.

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References

- Cheong, S.-W.; Mostovoy, M.V. Multiferroics: A magnetic twist for ferroelectricity. *Nat. Mater.* 2007, *6*, 13–20. [CrossRef] [PubMed]
 Fong, D.D.; Stephenson, G.B.; Streiffer, S.K.; Eastman, J.A.; Auciello, O.; Fuoss, P.H.; Thompson, C. Ferroelectricity in ultrathin
- perovskite films. *Science* 2004, *304*, 1650–1653. [CrossRef] [PubMed]
 Newnham, R.; Cross, L.E. Ferroelectricity: The foundation of a field from form to function. *MRS Bull.* 2005, *30*, 845–848. [CrossRef]
- Haertling, G.H. Ferroelectric ceramics: History and technology. J. Am. Ceram. Soc. 1999, 82, 797–818. [CrossRef]
- 5. I Kingon, A.; Srinivasan, S. Lead zirconate titanate thin films directly on copper electrodes for ferroelectric, dielectric and piezoelectric applications. *Nat. Mater.* **2005**, *4*, 233–237. [CrossRef]
- 6. Pulvari, C. Ferroelectrics and their memory applications. IRE Trans. Compon. Parts 1956, 3, 3–11. [CrossRef]
- Acosta, M.; Novak, N.; Rojas, V.; Patel, S.; Vaish, R.; Koruza, J.; Jrossetti, G.A.R.; Rödel, J. BaTiO₃-based piezoelectrics: Fundamentals, current status, and perspectives. *Appl. Phys. Rev.* 2017, 4, 041305. [CrossRef]
- 8. Gao, J.; Hu, X.; Wang, Y.; Liu, Y.; Zhang, L.; Ke, X.; Ren, X. Understanding the mechanism of large dielectric response in Pb-free (1– x) Ba (Zr_{0.2}Ti_{0.8}) O₃ x (Ba_{0.7}Ca_{0.3}) TiO₃ ferroelectric ceramics. *Acta Mater.* **2017**, *125*, 177–186. [CrossRef]
- 9. Jona, F.; Shirane, G. Ferroelectric Crystals; Dover Publications, Inc.: New York, NY, USA, 1993; Volume 11.

- Sakayori, K.-I.; Matsui, Y.; Abe, H.; Nakamura, E.; Kenmoku, M.; Hara, T.; Ishikawa, D.; Kokubu, A.; Hirota, K.-I.; Ikeda, T. Curie temperature of BaTiO₃. *Jpn. J. Appl. Phys.* **1995**, *34*, 5443–5445. [CrossRef]
- 11. Han, F.; Bai, Y.; Qiao, L.-J.; Guo, D. A systematic modification of the large electrocaloric effect within a broad temperature range in rare-earth doped BaTiO₃ ceramics. *J. Mater. Chem. C* **2016**, *4*, 1842–1849. [CrossRef]
- 12. Lin, F.; Shi, W. Effects of doping site and pre-sintering time on microstructure and magnetic properties of Fe-doped BaTiO₃ ceramics. *Phys. B Condens. Matter* **2012**, 407, 451–456. [CrossRef]
- 13. Yoon, M.-S.; Ur, S.-C. Effects of A-site Ca and B-site Zr substitution on dielectric properties and microstructure in tin-doped BaTiO₃–CaTiO₃ composites. *Ceram. Int.* **2008**, *34*, 1941–1948. [CrossRef]
- 14. Tsur, Y.; Dunbar, T.D.; Randall, C.A. Crystal and defect chemistry of rare earth cations in BaTiO₃. *J. Electroceramics* **2001**, *7*, 25–34. [CrossRef]
- Asbani, B.; Dellis, J.-L.; Lahmar, A.; Courty, M.; Amjoud, M.; Gagou, Y.; Djellab, K.; Mezzane, D.; Kutnjak, Z.; El Marssi, M. Lead-free Ba_{0.8}Ca_{0.2}(Zr_xTi_{1-x})O₃ ceramics with large electrocaloric effect. *Appl. Phys. Lett.* 2015, *106*, 042902. [CrossRef]
- 16. Langhammer, H.T.; Müller, T.; Felgner, K.-H.; Abicht, H.-P. Crystal structure and related properties of manganese-doped barium titanate ceramics. *J. Am. Ceram. Soc.* 2004, *83*, 605–611. [CrossRef]
- 17. Puli, V.S.; Li, P.; Adireddy, S.; Chrisey, D.B. Crystal structure, dielectric, ferroelectric and energy storage properties of La-doped BaTiO₃ semiconducting ceramics. *J. Adv. Dielectr.* **2015**, *5*, 1550027. [CrossRef]
- 18. Qian, X.-S.; Ye, H.-J.; Zhang, Y.-T.; Gu, H.; Li, X.; A Randall, C.; Zhang, Q.M. Giant electrocaloric response over a broad temperature range in modified BaTiO₃ ceramics. *Adv. Funct. Mater.* **2013**, *24*, 1300–1305. [CrossRef]
- 19. Luo, Z.-D.; Zhang, D.; Liu, Y.; Zhou, D.; Yao, Y.; Liu, C.; Dkhil, B.; Ren, X.; Lou, X. Enhanced electrocaloric effect in lead-free BaTi_{1-x}Sn_xO₃ ceramics near room temperature. *Appl. Phys. Lett.* **2014**, *105*, 102904. [CrossRef]
- Li, J.N.; Zhang, D.W.; Qin, S.Q.; Li, T.Y.; Wu, M.; Wang, D.; Bai, Y.; Lou, X.J. Large room-temperature electrocaloric effect in lead-free BaHf_xTi_{1-x}O₃ ceramics under low electric field. *Acta Mater.* 2016, 115, 58. [CrossRef]
- Rusevich, L.L.; Zvejnieks, G.; Kotomin, E.A.; Kržmanc, M.M.; Meden, A.; Kunej, S.; Vlaicu, I.D. Theoretical and experimental study of (Ba, Sr) TiO₃ perovskite solid solutions and BaTiO₃/SrTiO₃ heterostructures. *J. Phys. Chem. C* 2019, 123, 2031–2036. [CrossRef]
- 22. Devi, S.; Jha, A.K. Structural, dielectric and ferroelectric properties of tungsten substituted barium titanate ceramics. *Asian J. Chem.* **2009**, *21*, 117–124.
- 23. Arshad, M.; Du, H.; Javed, M.S.; Maqsood, A.; Ashraf, I.; Hussain, S.; Ma, W.; Ran, H. Fabrication, structure, and frequencydependent electrical and dielectric properties of Sr-doped BaTiO₃ ceramics. *Ceram. Int.* **2020**, *46*, 2238–2246. [CrossRef]
- 24. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *J. Acta Crystallogr. A* **1976**, *32*, 751–767. [CrossRef]