

LETTER TO THE EDITOR

A Simple Method for Judging Order or Disorder in $A(B'B'')O_3$ Perovskite Compounds

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A simple method for judging order or disorder distribution of the B' and B'' cation at the B site in $A(B'B'')O_3$ perovskite compounds is proposed. An order–disorder phase diagram is also given. The disorder region, order region, and order–disorder transition region in the diagram can be very well distinguished. The ordering or disordering in $A(B'B'')O_3$ can easily be determined by a simple calculation from some parameters of the B' and B'' cations and the A atom. © 1997 Academic Press

In an $A(B'B'')O_3$ -type perovskite compound, the distribution of the B' and B'' cations at the B site can be either random or regular. The two kinds of distributions can lead to disorder and order in $A(B'B'')O_3$ compounds. The arrangement of the ions in the lattice has a significant effect on some properties of the compound, such as the ferroelectric property. So research on ordering and disordering in $A(B'B'')O_3$ compounds has been very interesting.

Early, it was found that the larger the difference in the ionic radii or the charges of the B' and B'' cations, the larger the possibility of an ordered arrangement of the B' and B'' cations at the B site (1, 2). Relationships between some atomic parameters, such as electronegativity, and the order or disorder of structure have been studied (3). Some rules to judge order or disorder have been presented (4). Most of these criteria are qualitative. Recently, study of the order–disorder transition in $A(B'B'')O_3$ perovskite compounds by calculation of the Coulomb electrostatic interaction energy of the B -site ions has been reported (5, 6). Here, we give a simple method of judging order or disorder in $A(B'B'')O_3$ compounds.

In the cell of an ABO_3 perovskite, the A cations occupy the corner, the B cations occupy the center, and the oxygen anions are at the face-center of the cell. Six oxygen anions

around the B cation will form an octahedron. The octahedron will be distorted if the B' cation replaces the B'' cation in an octahedron. When the difference in shape and size of the octahedron with the B' and B'' cations is not very large, the distribution of the B' and B'' cations at the B site may be random, because the substitution of the B' for the B'' cation has no large effect on the stability of the structure. If the deformation of the octahedron is very large after substitution of the B' cation for the B'' cation, the occupancy of the B' and B'' cations at the B site will prefer to be in a certain way, so that their arrangement can stabilize the perovskite structure of the compound. The deformation of the octahedron caused by substitution depends not only on the difference in the ionic radii and the charges of the B' and B'' cations, but also on that in the polarizabilities of the B' and B'' cations, because the polarizability of an ion expresses the deformability of the ion under the action of the neighboring ions. The A cations at the corners of cell may also restrict the deformation of the octahedron. These will influence the ordering or disordering of the structure. So, first, we define two variables: $Y = \ln(100 \times |\Delta\alpha| / (N_A \times n_A))$ and $X = \ln(|Z_{B'}/r_{B'} - Z_{B''}/r_{B''}|)$. Here, $\Delta\alpha$ is the difference in the polarizabilities of the B' and B'' cations; $Z_{B'}/r_{B'}$ and $Z_{B''}/r_{B''}$ are the ratios of the charges to the ionic radii of the B' and B'' cations respectively; N_A and n_A are the largest principal quantum number and the number of total electrons in the outer electronic shells of the A atom, respectively. For example, $N_A = 6$ and $n_A = 2$ for the Ba atom and $N_A = 6$ and $n_A = 14$ for the Pb atom. Next, we calculated the values of Y and X for more than 60 $A(B'B'')O_3$ -type perovskite compounds. The effective ionic radii and the polarizabilities used in the calculations are from Refs. (7–9) respectively. In these compounds, $A = \text{Ca, Sr, Ba, Pb, La}$; $B' = \text{Li, Mg, Ca, Sr, Zn, Cd, Al, Fe, Co, Ni, Cr, Mn, Sc, Y, In, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu}$; $B'' = \text{Ir, Ru, Nb, Ta, W, Te}$. For better understanding of the relationship between order or disorder and the variables, in Fig. 1, Y is taken as the ordinate and X as the abscissa. In this way, the position of

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any $A(B'B'')O_3$ compound in the order–disorder phase diagram can be determined. As Fig. 1 shows, the ordered and disordered compounds will be in different regions of the diagram. If $X > 1.8$, the compound is ordered despite the value of Y . When $X < 1.8$, there exists a clear line of distinction between the order and disorder regions. The boundary between the order and disorder regions can be very well described by the linear function

$$Y_0 = -1.9X + 2.3. \quad [1]$$

In this case, we can determine whether any $A(B'B'')O_3$ compound is ordered. First, we calculate the values of Y and X for the compound according to the above definition. If $X > 1.8$, the compound must be ordered. If $X < 1.8$, then we must calculate the value of Y_0 at the boundary condition through formula [1] using the calculated X . We have noted that the region in $Y_0 \pm 0.3$ may be an order–disorder transition region. Hence, if $Y > Y_0 + 0.3$, the compound is ordered; if $Y < Y_0 - 0.3$, the compound is disordered; and if $Y_0 + 0.3 > Y > Y_0 - 0.3$, the compound will be in the order–disorder transition region or partly ordered. As Fig. 1 shows, the judgments for order or disorder of most of the compounds are in very good agreement with experimental results.

We have noted contradictory reports for the order of phases in $Pb(Ho_{1/2}Nb_{1/2})O_3$ (4, 5). Very interestingly, in the phase diagram, $Pb(Ho_{1/2}Nb_{1/2})O_3$ is just in the order–disorder transition region. The calculated result in Ref. (5) for $Pb(YbTa)O$ system indicates that the compound is ordered, and it disagrees with the experimental result. However, according to our calculation, the compound is disordered. The experiments have demonstrated that $Ba(Ni_{1/2}Nb_{1/2})O_3$ is disordered and $Ba(Ni_{1/3}Nb_{2/3})O_3$ is ordered (4, 10). Indeed, the two compounds are in different regions in the order–disorder phase diagram. $Pb(Mg_{1/3}Nb_{2/3})O_3$ is disordered and $La(Mg_{2/3}Nb_{1/3})O_3$ is ordered (11). From Fig. 1, one can find that this agrees with our judgment.

We have also noted contradictory conclusions as to order or disorder in some compounds, especially in the compounds of the order–disorder transition region. We consider that perhaps this is mainly because, in different synthesis processes, especially after heat treatment, some complicated changes in these compounds can happen, for example, changes in the content of oxygen, in the valence state of the metal ion, and even in the spin state of the metal ion. These changes can have important effects on order or disorder in the structure of the compound. We must point out that by our judgment method, only the atomic and ionic

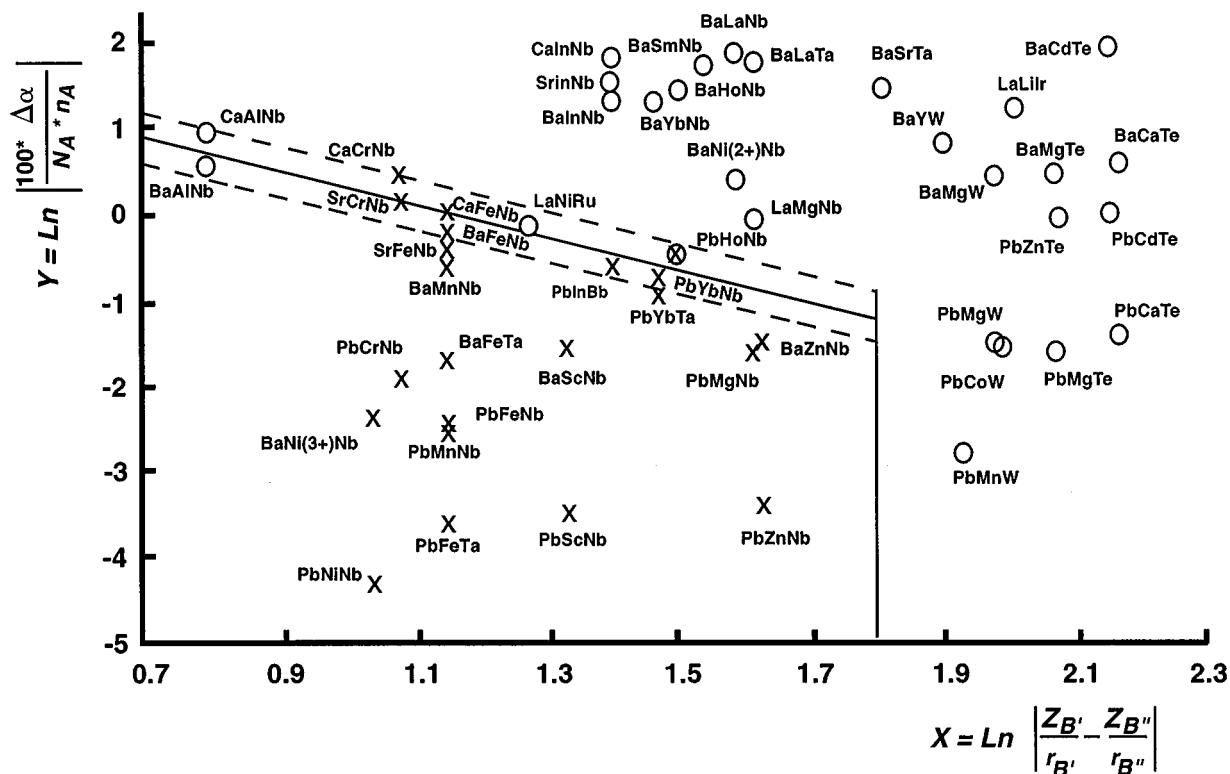


FIG. 1. The order–disorder phase diagram for $A(B'B'')O_3$ -type perovskite compounds. (X) disordered; (O) ordered.

parameters of the A , B' , and B'' are considered and the composition of compound must be $A(B'B'')O_3$. Any change in the heat treatment process has not been considered. We also emphasize that if the content of the B' or B'' cation in the compound is too small, it cannot create an independent phase or a sublattice in the crystal structure. So our method will be valid only for 1:1 and 1:2 (2:1) ordered compounds. As for so-called 1:3 ordered compounds, not only are these compounds very rare, but also it is doubtful if there exists any ordered arrangement of the B' and B'' cations in these compounds (12).

In summary, a simple method has been proposed to judge if there exists an ordered or disordered arrangement of the B' and B'' cations at the B site in an $A(B'B'')O_3$ perovskite compound through simple calculation using some parameters of the B' and B'' cation and the A atom. This method is valid for the 1:1 and 1:2 (2:1) ordered compounds. It can be used to predict whether unknown perovskite compounds with a formula $A(B'B'')O_3$ may be ordered.

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REFERENCES

1. F. Galasso, L. Katz, and R. Ward, *J. Am. Chem. Soc.* **81**, 820 (1959).
2. F. Galasso and W. Darby, *J. Phys. Chem.* **66**, 131 (1962).
3. C. A. Randail, A. S. Bhalla, T. R. Shrout, and L. E. Cross, *J. Mater. Res.* **4**, 829 (1990).
4. N. Setter and L. E. Cross, *J. Mater. Sci.* **15**, 2478 (1980).
5. X. W. Zhang, Q. Wang, and B. L. Gu, *J. Am. Ceram. Soc.* **74**, 2846 (1991).
6. H. Gui, B. L. Gu, and X. W. Zhang, *J. Am. Ceram. Soc.* **79**, 381 (1996).
7. R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
8. Y. Q. Jia, *J. Solid State Chem.* **95**, 184 (1991).
9. X. Z. You, *Kexue Tongbao* **9**, 419 (1974). [in Chinese]
10. B. K. Kim, H. Hamaguchi, I. T. Kim, and K. S. Hong, *J. Am. Ceram. Soc.* **78**, 3117 (1995).
11. L. J. Lin and T. B. Wu, *J. Am. Ceram. Soc.* **74**, 1360 (1991).
12. I. S. Kim, T. Nakamura, M. Itoh, and Y. Inagoma, *Mater. Res. Bull.* **28**, 1029 (1993).