Chinese Chemical Letters Vol. 11, No. 8, pp. 747–748, 2000

Chemical Bond Parameters in Sr_3MRhO_6 (M=Rare earth)

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Abstract: Chemical bond parameters, that is, bond covalency, bond valence, macroscopic linear susceptibility, and oxidation states of elements in Sr_3MRhO_6 (M=Sm, Eu, Tb, Dy, Ho, Er, Yb) have been calculated. The results indicate that the bond covalency of M-O decreases sharply with the decrease of ionic radius of M^{3+} from Sm to Yb, while no obvious trend has been found for Rh-O and Sr-O bonds. The global instability index indicates that the crystal structures of Sr_3MrhO_6 (M = Sm, Eu, Tb, Dy, Ho) have strained bonds.

Keywords: Chemical bond parameters, Sr_3MRhO_6.

Over the years, the concept of bond covalency or ionicity has been proved to be a very important quantity in classifying and explaining many basic properties of molecules and solids from the viewpoint of the electronic structure. Nevertheless, previous study in this aspect was only on binary crystals, which limited the usefulness of the theory. The recently proposed method [1] for the evaluation of chemical bond parameters including bond covalency has made the study on crystals with multiple bonds possible. In this paper, the method has been applied to the study of Sr_3MRhO_6 (M = Sm, Eu, Tb, Dy, Ho, Er, Yb)[2]. These materials have been recently synthesized and have K_4CdCl_6 structure type. They attracted much attention due to their interesting structural and magnetic properties.

The theoretical method can be found elsewhere [1] and will not be given in this paper. The bond valence scheme (bvs) [3] was adopted in the calculation of bond valence and oxidation states of elements. The bond valence parameters were taken from ref. 3.

According to crystallographic data [2] and the theoretical method, Sr_3MRhO_6 can be decomposed into the sum of binary crystals as follows

$$Sr_3MRhO_6 = Sr(1)_3M(1)Rh(1)O(1)_6$$
$$= Sr_3O_4 + MO + RhO$$

From **Table 1**, it can be seen that the bond covalency of M-O decreases sharply with the decrease of ionic radii of M^{3+} from Sm to Yb, while no obvious trend was observed for Rh-O and Sr-O bonds. The trend is also not obvious for the bond valence from Sm to Yb, but for a given compound (fixed M), the magnitude of bond valence has the following order, M-O>Rh-O>Sr-O except for M=Yb, in which Rh-O>M-O>Sr-O. For the valence of elements, we notice that the valence of rare earth is around +3.0,

except Eu, which deviates a little bit large from +3.0. In contrast, the valence of Rh is much smaller than its normal valence +3.0 except for M = Er, Yb. These relatively small valences can be ascribed to the longer bond distances [2] (and therefore less bond valences according to bvs) of the corresponding bonds. The magnitude of macroscopic linear susceptibility decreases with the decrease of ionic radius of M^{3+} from Sm to Yb. It is known that [4] larger values of global instability index R1 are indicative of strained bonds which can lead to instability in the crystal structure. For unstrained structure R1 < 0.1 v.u., but for compounds with lattice-induced strains R1 can be as large as 0.2 v.u. Crystal structures with R1 > 0.2 v.u. were generally found to be either incorrect or refined in a space group with too high symmetry. From our calculation of global instability index R1, we can infer that the crystal structures for M = Sm, Eu, Tb, Dy, and Ho have strained bonds, and the structure for M = Eu even has a R1 as large as 0.23, which may indicate that the structure of Sr_3EuRhO_6 is unstable.

Table 1 Bond covalency (b.c., in %), bond valence (b.v.), oxidation states of elements (o.s.), global instability index (R1) and macroscopic linear susceptibility (χ) in Sr_3MRhO_6 (M = Sm, Eu, Tb, Dy, Ho, Er, Yb)

	Sm	Eu	Tb	Dy	Ho	Er	Yb
b. c.							
M - O	18.21	13.01	8.25	6.67	5.44	4.58	3.00
Rh - O	13.58	13.44	13.77	13.76	13.74	14.13	12.86
Sr - O	3.60	3.76	3.54	3.62	3.63	3.53	3.35
b. v.							
M - O	0.5061	0.4373	0.5313	0.5020	0.4873	0.4993	0.4667
Rh - O	0.4211	0.4055	0.4481	0.4315	0.4421	0.4912	0.4769
Sr - O	0.2492	0.2633	0.2473	0.2491	0.2554	0.2479	0.2563
o. s.							
M	3.037	2.624	3.188	3.012	2.924	2.996	2.800
Rh	2.527	2.433	2.689	2.589	2.653	2.947	2.861
Sr	1.994	2.106	1.978	1.993	2.043	1.983	2.051
O	1.924	1.896	1.969	1.930	1.951	1.982	1.969
R1	0.15	0.23	0.11	0.13	0.12	0.02	0.08
χ	1.139	0.891	0.672	0.588	0.508	0.474	0.318

Acknowledgments

Authors thank the financial support of the National Natural Science Foundation of China (Grant No. 29871029).

References

1. Z. J. Wu, Q. B. Meng, S. Y. Zhang, *J. Phys. Chem., A* **1999**, *103*(21), 4270.
2. R. C. Layland, S. L. Kirkland, H. -C. zur Loye *J. Solid State Chem.*, **1998**, *139*, 79.
3. N. E. Brese, M. O'Keeffe, *Acta Crystallogr. B*, **1991**, *47*, 192.
4. I. D. Brown, *Acta Crystallogr. B*, **1992**, *48*, 553.

Received 25 October 1999
Revised 19 June 2000