Journal of Solid State Chemistry 196 (2012) 574–578

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

# Correlation among electronegativity, cation polarizability, optical basicity and single bond strength of simple oxides

Vesselin Dimitrov [a], Takayuki Komatsu [b],*

[a] Department of Silicate Technology, University of Chemical Technology and Metallurgy, 8, Kl. Ohridski Blvd., Sofia 1756, Bulgaria
[b] Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka-cho, Nagaoka 940-2188, Japan

ARTICLE INFO

*Article history:*
Received 1 June 2012
Received in revised form
13 July 2012
Accepted 15 July 2012
Available online 22 July 2012

*Keywords:*
Polarizability
Electronegativity
Optical basicity
Simple oxide
Single bond strength

ABSTRACT

A suitable relationship between free-cation polarizability and electronegativity of elements in different valence states and with the most common coordination numbers has been searched on the basis of the similarity in physical nature of both quantities. In general, the cation polarizability increases with decreasing element electronegativity. A systematic periodic change in the polarizability against the electronegativity has been observed in the isoelectronic series. It has been found that generally the optical basicity increases and the single bond strength of simple oxides decreases with decreasing the electronegativity. The observed trends have been discussed on the basis of electron donation ability of the oxide ions and type of chemical bonding in simple oxides.

## 1. Introduction

Electronic polarizability of ions demonstrates the easy deformation of their electronic clouds by applying an electromagnetic field. It is an important parameter because it is closely related to many properties of the solids such as refraction, conductivity, ferroelectricity, electro-optical effect, optical nonlinearity along with optical basicity [1–3]. Electronic polarizability $\alpha$ of an atom or ion could be given through a one-dimensional Hooke's-law potential energy by

$$\alpha = e^2 \sum \frac{n_i}{k_i} \tag{1}$$

where $e$ is the elementary charge and $n_i$ is the number of electrons with binding force constant $k_i$ [4]. According to this model, Hooke's-law potential energy is assumed to be equal to the ionization energy $IE$ as twice the value of effective ionic radii, $2r_{\text{eff}}$. By this manner electron binding force constant $k_i$ can be given by

$$k = \frac{IE}{2r_{eff}^2} \tag{2}$$

or electronic ion polarizability is

$$\alpha = 2e^2 r_{eff}^2 \sum \frac{n_i}{IE} \tag{3}$$

As can be seen the loosely bound valence electrons with low ionization energy, i.e., small force constant will contribute more to the electronic polarizability of an atom or ion than the tightly bound inner-shell electrons. Recently, Dimitrov and Komatsu [5] have found suitable relationship between free-ion polarizability and element outermost binding energy on the basis of the similarity in physical nature between electron binding energy and ionization energy. It has been suggested that outermost core-level binding energy can be used for relative measure of the cation polarizability. In general, cation polarizability increases with decreasing element binding energy. Simultaneously, a systematic periodic change in the polarizability against the binding energy has been observed in the isoelectronic series [5].

On the other hand, the element electronegativity demonstrates the ability of an atom or ion to attract electrons from the atoms or ions bonded to it. Also recently, Li and Xue [6] have published electronegativities of 82 elements in different valence states and with the most common coordination numbers calculated on the basis of an effective ionic potential defined by the ionization energy and ionic radii. The following equation for the electronegativity $\chi_i$ has been proposed:

$$\chi_i = 0.105 n^* \left(\frac{I_{\text{m}}}{R_\infty}\right)^{1/2} \left(\frac{1}{r_{\text{i}}}\right) + 0.863 \tag{4}$$

---

* Corresponding author. Fax: +81 258 47 9300.
*E-mail addresses:* vesselin@uctm.edu (V. Dimitrov), komatsu@mst.nagaokaut.ac.jp (T. Komatsu)

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2012.07.030

where $n^*$ is the effective principal quantum number, $R_\infty$ is the Rydberg constant, $I_m$ is the ionization energy and $r_i$ is the ionic radii.

Li and Xue [6] have discussed that the Lewis acid strength can be quantitatively measured as a function of their electronegativity scale. The Lewis acid strength $S_a$ has been introduced by Brown [7] to predict which Lewis acids will bond to which Lewis bases. It is defined for a given cation by

$$S_a = \frac{V}{N_t} \tag{5}$$

where $V$ is the oxidation state of the cation and $N_t$ is the average of the coordination numbers to oxygen observed in a large sample of compounds [8]. Brown and Skowron [8] have established that for main group elements in their highest oxidation state a scale of Lewis acid strength derived from observed structures correlates with a scale of electronegativity derived from electron energies in the free atom.

Eqs. (3) and (4) show that the physical origin of electronic ion polarizability and electronegativity obtained by Li and Xue is very similar, since both of them are related to the ionization energy and ionic radii. Therefore, it is of interest to check the correlation between these quantities. That is why in this paper we have examined the relationship between electronegativity and electronic polarizability of different ions. The relationship with optical basicity as well as single bond strength of numerous simple oxides is also discussed.

## 2. Results and discussion

### 2.1. Dependence of cation polarizability on electronegativity

A couple of sets of free-ion polarizabilities have been proposed by Pauling [9], Born and Heisenberg [10], Fajans and Joos [11], Mayer and Mayer [12] and Kordes [13], The most comprehensive sets among them are those proposed by Pauling [9] and Kordes [13]. Pauling's values have been obtained on a theoretical treatment of the quadratic Stark effect by means of the following equation:

$$R = 0.047n^4(15n^2+21)\sum\frac{1}{(Z-S_R)^4} \tag{6}$$

$R$ is the ionic refraction, $n$ is the principal quantum number, $Z$ is the electron number and $S_R$ is the mole refraction screening constant.

On the other hand, Kordes [13] has calculated the free-ion polarizabilities on the basis of ionic radii by the equation

$$\left[\left(\frac{R}{0.603}\right)^{1/3}\right]^{2/3} = kr_u = kr_z Z^{2/(n_B-1)} \tag{7}$$

where $r_u$ is the univalent crystal radii, $r_z$ is the actual crystal radii, $n_B$ is the Born repulsion exponent and $k$ is the constant. The cation polarizabilities of ions under consideration in this paper obtained by Pauling and by Kordes are presented in Table 1 (columns 3 and 4). As can be seen a good correspondence exists between two independently obtained sets. In the present study we used polarizability data reported by Kordes (Table 1, column 3) which we have been used in our previous papers [5,14–17]. Recently, condensed phase ionic polarizabilities from plane wave density functional theory calculation were reported by Heaton et. al. [18] which are in good agreement with the polarizabilities used by Dimitrov and Sakka [14] for a free ion [13]. In column 6 of Table 1 the values of element electronegativity according to Li and Xue [6] are listed, taking into account the valence state of cation and its most common coordination number in the oxides. On the basis of the data presented in Table 1, it is possible to investigate the change in the polarizability of the cations with electronegativity through classification based on their outermost electron configuration. In this connection the data of cation polarizability are plotted as a function of element electronegativity in Fig. 1. As can be observed there is systematic periodic change in the cation polarizability and related element electronegativity. Cation polarizability increases and electronegativity decreases in all series. Therefore, from electronegativity point of view the increase in the cation polarizability in each series means decreased ability of an ion to attract electrons from the atoms bonded to it. The observed good correlation between cation polarizability and element electronegativity in isoelectronic series could be explained taking into consideration their common physical ground. As can be seen in Eqs. (3) and (4) both quantities are related to the ionization energy and ionic radii. Similar trend as that shown in Fig. 1 has been found studying the relationship between cation polarizability and element binding energy based on the similarity in physical nature between electron binding energy and ionization energy [5].

**Table 1**
Ion, outermost electron orbital, cation polarizability ($\alpha_i$), coordination number (CN) and electronegativity ($\chi_i$).

| Ion | Outermost orbital | $\alpha_i$ (Å$^3$; Kordes) | $\alpha_i$ (Å$^3$; Pauling) | CN | $\chi_i$ (Li and Xue) |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| $B^{3+}$ | $1s^2$ | 0.002 | 0.003 | 3 | 3.189 |
| $Be^{2+}$ | $1s^2$ | 0.007 | 0.008 | 4 | 1.453 |
| $Li^+$ | $1s^2$ | 0.024 | 0.029 | 4 | 1.043 |
| $P^{5+}$ | $2p^6$ | 0.021 | 0.021 | 4 | 3.003 |
| $Si^{4+}$ | $2p^6$ | 0.033 | 0.033 | 4 | 2.245 |
| $Al^{3+}$ | $2p^6$ | 0.054 | 0.054 | 6 | 1.513 |
| $Mg^{2+}$ | $2p^6$ | 0.094 | 0.094 | 6 | 1.234 |
| $Na^+$ | $2p^6$ | 0.175 | 0.181 | 6 | 1.024 |
| $Cr^{6+}$ | $3p^6$ | 0.085 | 0.087 | 6 | 2.475 |
| $V^{5+}$ | $3p^6$ | 0.122 | 0.123 | 6 | 2.030 |
| $Ti^{4+}$ | $3p^6$ | 0.184 | 0.187 | 6 | 2.278 |
| $Sc^{3+}$ | $3p^6$ | 0.287 | 0.290 | 6 | 1.415 |
| $Ca^{2+}$ | $3p^6$ | 0.469 | 0.472 | 8 | 1.132 |
| $K^+$ | $3p^6$ | 0.821 | 0.841 | 9 | 0.987 |
| $Se^{6+}$ | $3d^{10}$ | 0.073 | 0.075 | 4 | 2.977 |
| $As^{5+}$ | $3d^{10}$ | 0.100 | 0.103 | 4 | 2.499 |
| $Ge^{4+}$ | $3d^{10}$ | 0.137 | 0.143 | 4 | 2.116 |
| $Ga^{3+}$ | $3d^{10}$ | 0.195 | 0.198 | 4 | 1.755 |
| $Zn^{2+}$ | $3d^{10}$ | 0.283 | 0.286 | 4 | 1.426 |
| $Mo^{6+}$ | $4p^6$ | 0.169 | 0.190 | 6 | 2.101 |
| $Nb^{5+}$ | $4p^6$ | 0.242 | 0.262 | 6 | 1.862 |
| $Zr^{4+}$ | $4p^6$ | 0.357 | 0.377 | 8 | 1.518 |
| $Y^{3+}$ | $4p^6$ | 0.544 | 0.560 | 8 | 1.291 |
| $Sr^{2+}$ | $4p^6$ | 0.861 | 0.865 | 8 | 1.123 |
| $Rb^+$ | $4p^6$ | 1.437 | 1.417 | 10 | 0.987 |
| $Te^{6+}$ | $4d^{10}$ | 0.242 | 0.262 | 6 | 2.180 |
| $Sb^{5+}$ | $4d^{10}$ | 0.333 | 0.361 | 6 | 1.971 |
| $Sn^{4+}$ | $4d^{10}$ | 0.479 | 0.500 | 6 | 1.706 |
| $In^{3+}$ | $4d^{10}$ | 0.662 | 0.730 | 6 | 1.480 |
| $Cd^{2+}$ | $4d^{10}$ | 1.054 | 1.087 | 6 | 1.276 |
| $Ce^{4+}$ | $5p^6$ | 0.702 | 0.738 | 6 | 1.608 |
| $La^{3+}$ | $5p^6$ | 1.052 | 1.048 | 7 | 1.301 |
| $Ba^{2+}$ | $5p^6$ | 1.595 | 1.563 | 8 | 1.115 |
| $W^{6+}$ | $4f^{14}$ | 0.147 | – | 6 | 2.175 |
| $Ta^{5+}$ | $4f^{14}$ | 0.185 | – | 6 | 1.925 |
| $Hf^{4+}$ | $4f^{14}$ | 0.368 | – | 6 | 1.706 |

### 2.2. Dependence of optical basicity of simple oxides on element electronegativity

The estimation of the electronic polarizability of ions is subject to the so-called polarizability approach in the materials science, which is well known especially in the field of glass science [19]. The polarizability approach has been systematically developed in our recent papers concerning the origin of electronic polarizability