Dielectric constants of binary rare-earth compounds

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Abstract. The dielectric constants of rare-earth oxides (RE_2O_3) and rare-earth nitrides, phosphides, arsenides, and antimonides (REX, RE = rare-earth element, X = N, P, As, Sb) are quantitatively estimated. The estimation is based on the approximately linear relationship between the dielectric constant and the atomic number of the constituent atoms. Similar correlations are valid in nearly all series of related compounds; thus the approach presented here can be used as an effective tool in the search for materials with specific properties, e.g. high dielectric constants.

1. Introduction

The dielectric constant of a material is one of the key parameters for device design in nearly all fields of modern electronics. Furthermore, it is of fundamental importance for the behaviour of charge carriers, dopants, defects, and impurities in insulators and semiconductors. Many efforts with different starting points have been made in order to find good calculatory procedures for the linear dielectric responses of crystal materials. These include ones based on the density of inorganic solid substances [1], the interionic separations [2], the bond-orbital theory for ionic crystals [3], dielectric polarizabilities of constituent ions [4], the dielectric theory of chemical bonds for solids [5,6], the average atomic number of constituent atoms of crystals [7,8], and the band structures of the alkali halides [9]. Yet to date no universal method has been established for the determination of the linear dielectric response for any substance. We therefore in the current work explore a new method for correlating linear dielectric response and constituent atoms of crystal materials.

In their recent work, Park *et al* [10] proposed a novel approach for identifying highly dielectric materials, using the Clausius–Mossotti equation

$$\varepsilon = \left(V_m + 2\alpha_D \frac{4\pi}{3} \right) \Big/ \left(V_m - \alpha_D \frac{4\pi}{3} \right) \tag{1}$$

which provides a direct relationship between the dielectric constant, ε, the molecular dielectric polarizability, α_D, and the molar volume, V_m, of a material. They explain that the Clausius–Mossotti equation, the oxide additivity rule (i.e., the molecular dielectric polarizability, α_D, can be calculated by summing the polarizabilities of the constituent ions), and known polarizabilities of individual ions [4] can be used in combination as a powerful tool for predicting the dielectric constant of hypothetical materials, provided that the molar volume can be accurately estimated. They further derive from the Clausius–Mossotti equation that decreasing the molar volume V_m will directly increase the dielectric constant.

We will show in the present work that in certain cases a counter-effect takes place which in fact *decreases* the dielectric constant with decreasing molar volume.

The present paper is an extension of earlier work [6], where the dielectric constants of some REX crystals of the rock-salt structural type were quantitatively calculated using the dielectric theory of chemical bonds for solids. More recent work [11] has shown that this theory is a widely applicable method in calculating or predicting dielectric responses of crystal materials. However, one of the most important aspects of this method is that the detailed crystal structures of the materials to be studied must be clearly known. More interesting data could be provided if one could reasonably extend the results obtained by calculations beyond the domain of known structural data. The current work will deal with this matter; it starts from the most fundamental parameters of the constituent atoms of crystal materials—i.e., the corresponding atomic numbers for constituent atoms or ions.

It should be emphasized, however, that the method described and applied here is fully applicable only to crystal series exhibiting a uniform crystal symmetry. Special care has to be taken when dealing e.g. with soft-mode-controlled systems—as in the case of various perovskite families. In this case the application of the method must be restricted to temperature ranges where all members of the respective family exhibit the same symmetry and where soft-mode-enhanced features like huge dielectric constants do not play any role.

2. Theoretical basis

Previous works [7, 8] have shown that the dielectric constants of solid-state compounds are correlated with the average atomic number of the constituent atoms Z_{av}. This is based on the fact that the dielectric constant of a solid, ε, may be expressed in terms of the polarizability of its constituent atoms, α_i:

$$\varepsilon = 1 + \left[\left(\sum N_i \alpha_i / \varepsilon_0 \right) \Big/ \left(1 - \sum \gamma N_i \alpha_i / \varepsilon_0 \right) \right] \tag{2}$$

where N_i is the number of atoms of species i per unit volume, ε_0 is the free-space permittivity, and γ is the Lorentz factor. Since α_i may be considered to be linearly related to the atomic number Z, the dielectric constant, ε, may be expressed as [7]

$$\varepsilon = (a - b Z_{av})^{-1} \qquad \text{or} \qquad \varepsilon = a' - b' Z_{av} \tag{3}$$

where a and b or a' and b', respectively, are constant for each group of solids; Z_{av} is defined as the mean of the corresponding atomic numbers of the constituent atoms. For the case of e.g. $A_x B_y$-type compounds, $Z_{av} = (x Z_A + y Z_B)/(x + y)$. If in a series of compounds one of the constituents, e.g. B, and x and y remain fixed, the linear dependence of equation (3) may be further simplified to

$$\varepsilon = a'' - b'' Z_A. \tag{4}$$

3. Results and discussion

The ion polarizabilities α_D and the modified crystal ionic radii r for the rare-earth ions have been calculated by Shannon [4] and Grimes and Grimes [12], respectively; their data are summarized in figure 1. To a good approximation both the modified crystal ionic radius and the polarizability depend linearly on the atomic number of the respective ion. This validates our approach discussed above of assuming a simplified linear dependence for the dielectric constants for each series of binary rare-earth compounds.
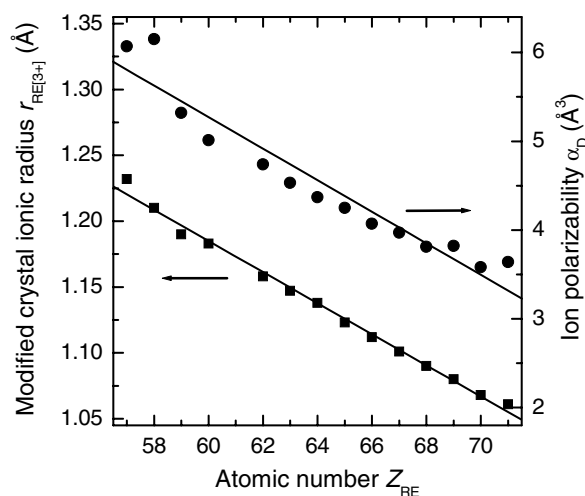
Figure 1. Modified ion radius and calculated polarizability for 3+ rare-earth ions (data taken from reference [12]). Lines represent linear fits to the data.

For the rare-earth oxides RE_2O_3 some experimental data for the dielectric constants are available [13]. They are plotted as a function of the atomic number of the participating rare-earth ion in figure 2. On the basis of the deduced linear correlation, the missing data can be calculated. The final results are listed in table 1.
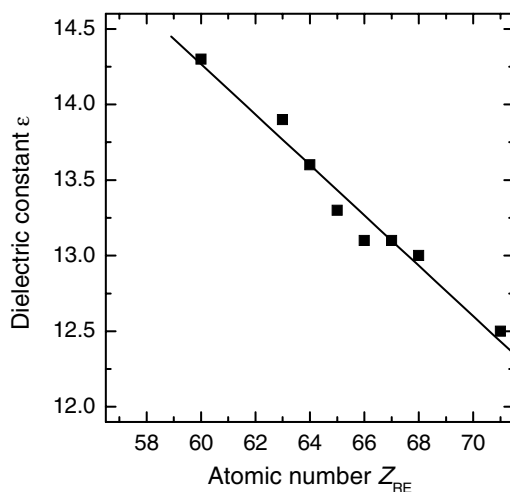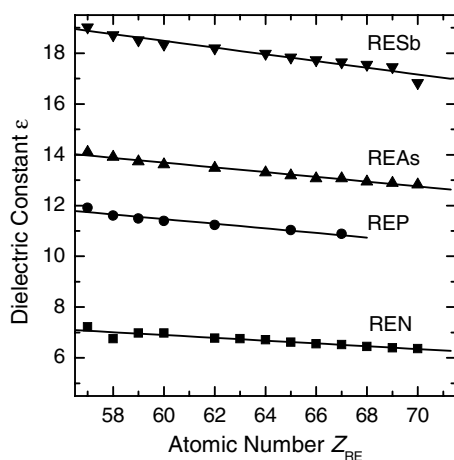

Figure 2. Dielectric constants of rare-earth oxides RE_2O_3 (RE = Lu, Er, Ho, Dy, Tb, Gd, Eu, and Nd) as a function of the rare-earth atomic number (experimental data taken from [13]).

If we take the available calculated linear dielectric constants ε of some REX crystals from the previous work [6], again an approximately linear dependence on the atomic number can be obtained (figure 3). Obviously, we can reasonably describe the relationship between the dielectric constant and the atomic number of the rare-earth ion in each REX crystal series (where X = N, P, As, Sb) as a straight linear dependence. Values which are missing due to a lack of exact structural data can be easily calculated using this relationship. The data for

Table 1. Dielectric constants ε of rare-earth oxides RE_2O_3; comparison between experimental values and data derived on the basis of the linear model discussed here.

Compound	Z_{RE}	ε_{exp} [12]	ε_{calc} (this work)
La_2O_3	57		14.77
Ce_2O_3	58		14.60
Pr_2O_3	59		14.43
Nd_2O_3	60	14.3	14.27
Pm_2O_3	61		14.10
Sm_2O_3	62		13.93
Eu_2O_3	63	13.9	13.77
Gd_2O_3	64	13.6	13.60
Tb_2O_3	65	13.3	13.43
Dy_2O_3	66	13.1	13.27
Ho_2O_3	67	13.1	13.10
Er_2O_3	68	13.0	12.93
Tm_2O_3	69		12.77
Yb_2O_3	70		12.60
Lu_2O_3	71	12.5	12.43

Figure 3. Dielectric constants of various rare-earth nitrides (REN), phosphides (REP), arsenides (REAs), and antimonides (RESb). Points represent data taken from reference [6]; lines are linear fits to these data.

all REX crystals calculated in this way are summarized in table 2. A comparison between the published experimental value for the dielectric constant of GdP ($\varepsilon_{exp} = 11.2$) [14] and our calculated value ($\varepsilon_{calc} = 11.1$) shows that our current method is quite reasonable and can give us a useful guide in calculating and predicting the linear dielectric constants of crystal materials.

On the other hand, again an approximately linear correlation between dielectric constant and crystal constituent ions is obtained when the dielectric constants of REX crystals are plotted versus the atomic number Z_X of the anion X. This shows that equation (4) is quite explicit in describing the relationship between dielectric constant and crystal composition for binary REX and related compounds. On the basis of the linearized model discussed here, dielectric constants may also be calculated for mixed rare-earth compounds of the type $RE^{(1)}_{1-x}RE^{(2)}_{x}X^{(1)}_{1-y}X^{(2)}_{y}$.

Table 2. Linear dielectric constants ε of all rare-earth nitrides (REN), phosphides (REP), arsenides (REAs), and antimonides (RESb). Values calculated in a previous report [6] and values derived on the basis of a linearized model are given.

	REN		REP		REAs		RESb	
	Reference [6]	This work	Reference [6]	This work	Reference [6]	This work	Reference [6]	This work
La	7.22	7.07	11.91	11.74	14.10	13.97	19.02	18.88
Ce	6.75	7.01	11.60	11.65	13.91	13.88	18.72	18.75
Pr	6.98	6.96	11.49	11.56	13.73	13.78	18.52	18.62
Nd	6.98	6.90	11.39	11.47	13.61	13.69	18.35	18.49
Pm		6.85		11.37		13.60		18.35
Sm	6.78	6.79	11.23	11.28	13.48	13.50	18.20	18.22
Eu	6.75	6.74		11.19		13.41		18.09
Gd	6.71	6.68		11.10	13.30	13.32	17.99	17.96
Tb	6.62	6.63	11.03	11.01	13.18	13.22	17.84	17.82
Dy	6.55	6.57		10.92	13.06	13.13	17.73	17.69
Ho	6.52	6.51	10.88	10.83	13.06	13.03	17.65	17.56
Er	6.45	6.46		10.74	12.94	12.94	17.55	17.43
Tm	6.39	6.40		10.65	12.88	12.85	17.46	17.29
Yb	6.36	6.35		10.56	12.82	12.75	16.83	17.16
Lu		6.29		10.46		12.66		17.03

Figures 2 and 3 show that the values of the linear dielectric constants of all rare-earth compounds examined here decrease with increasing atomic number of the rare-earth element. The atomic radius and the molar volume V_m also decrease with increasing atomic number in all series studied (figure 1 and reference [6]). Obviously in all of these compounds a decrease of the molar volume leads to a decrease in the ion polarizability, probably due to an increasing bond strength for electrons responsible for this polarizability. This finding contrasts with the assumptions made by Park *et al* [10] who assume that a decrease in the molar volume leads to an increase in the dielectric response.

4. Summary and conclusions

Dielectric constants of binary rare-earth compounds including all RE_2O_3- and REX-type crystals have been studied on the basis of the approximately linear correlation between dielectric constant and crystal composition. We were able to show that in series of similar crystals, physical properties like the dielectric constant to a good approximation depend linearly on the atomic number of the varying ion type. This facilitates the determination of the properties of crystals not yet synthesized. The method presented here will be helpful to materials scientists for finding new materials with desired dielectric properties among series of structurally similar materials. The present work presents a powerful tool for modifying the dielectric response of target materials by changing their compositions—that is to say, the change in coordination environment of constituent ions of a selected crystal family will finally lead to corresponding changes in dielectric responses of materials.

Furthermore, we found that in the compounds investigated here, the dielectric response decreases with decreasing molar volume. Taking the Clausius–Mossotti equation (equation (1)) as a basis for the derivation of ε, one should carefully consider the influence of both molar volume *and* molecular polarizability. Often a reduction in molar volume is combined with a tighter binding in the electron system, which in turn reduces the polarizability.

Acknowledgment

References

[1] Sangwal K and Kucharczyk W 1987 *J. Phys. D: Appl. Phys.* **20** 522
[2] Sharma S B, Paliwal P and Kumar M 1990 *J. Phys. Chem. Solids* **51** 35
[3] Lines M E 1990 *Phys. Rev.* B **41** 3372
[4] Shannon R D 1993 *J. Appl. Phys.* **73** 348
[5] Samanta L K and Chatterjee S 1994 *Phys. Status Solidi* b **182** K85
[6] Zhang S 1995 *Chinese J. Rare Earths* **13** 85
[7] Nag B R 1994 *Appl. Phys. Lett.* **65** 1938
[8] Marquez R and Rincon C 1995 *Phys. Status Solidi* b **191** 115
[9] Johannsen P G 1997 *Phys. Rev.* B **55** 6856
[10] Park J H, Parise J B, Woodward P M, Lubomirsky I and Stafsudd O 1999 *J. Mater. Res.* **14** 3192
[11] Xue D and Zhang S 1999 *Physica* B **262** 78
[12] Grimes N W and Grimes R W 1998 *J. Phys.: Condens. Matter* **10** 3029
[13] Shannon R D, Subramanian M A, Allik T H, Kimura H, Kokta M R, Randles M H and Rossman G R 1990
       J. Appl. Phys. **67** 3798
[14] Guntherodt G and Wachter P 1974 *Proc. 11th Rare Earth Research Conf.* vol 2, p 820