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Dielectric constant dependence on atomic substitution of Y_2BaCuO_5 clarified by ab initio calculations

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Abstract

The improvement of the microwave properties is an important goal to increase the performance and application of communication devices. The aim of this paper is to clarify the dependence of the dielectric constant and lattice constants of the Y_2BaCuO_5, with space group *Pbnm* 62 with substitution of Zn or Ni for Cu on the C-site and Sr for Ba on the B-site and Nd or others for Y on the A-site. With ab initio calculations the density of states and the electronic band structure was calculated for different substitutions and compared to experimental data. Tracking electronic bands indicate a high dielectric constant, which is the case for the Y_2BaCuO_5 series, in good agreement with published experimental data. Further analysis of the electronic band structure, like band gap, and direct transition path showed the quantitative agreement to the experimental data and allows some predictions for improving the Y_2BaCuO_5 based microwave materials.

Keywords: Y_2O_2-based ceramics; Transition metal oxide; Dielectric properties; Electric properties

1. Introduction

The performance of microwave resonators can be improved, when the dielectric constant, ε, the quality factor, Q_f is enhanced or the temperature coefficient of the resonant frequency, τ_f decreased. The present study has the aim to check, whether the dielectric constant can be predicted by a electronic band structure simulation[1] rather than the common ab initio approach by phonon calculations of the polarization.[2–7] This study focus on transition metal/rare earth oxides series based on the insulator Y_2BaCuO_5 (Y2115)[8–14] with space group *Pbnm* (No. 62),[15] which have been studied systematically in different solid-solutions by substituting the elements on A-side ($Y_{2-x}Nd_xBaCuO_5$[11,12]), B-side ($Y_2Ba_xSr_{1-x}CuO_5$[10]) or C-side ($Y_2BaCu_{1-x}Zn_xO_5$[8] $Y_2BaCu_{1-x}Ni_xO_5$.[9] When Y is fully substituted by Nd as in Nd_2BaZnO_5, the crystal structure becomes tetragonal with space group *I4/mcm* (140),[14] which is not considered here. Studies on the high T_C superconductors $YBa_2Cu_3O_7$ (Y123) with *Pmmm* (47) structure,[16] and $YBa_2Cu_4O_8$ with *Ammm* (65)[17] lead to the conclusion, that a higher bond valence corresponds to a stronger bonding strength and decreases the temperature coefficient of the resonant frequency.[18,19] While calculations of the quality factor[20,21] on different perovskites point out the importance of the phonon contribution, this study based on band structure calculations is restricted on the prediction of the dielectric constant of Y_2BaCuO_5.

For prediction of properties of new materials, the crystal structure has to be known as well. The linear dependence of the lattice constant of a solid solution is fulfilled in the case of Y_2BaCuO_5-series, showing the validity of the Vegard rule, which correlates the atomic concentration and the effective ion radius to volume of the unit cell. However, due to the strong bonding in atomic coordination polyeder, namely the NiO_5-polyeder with Ni–O bond of 0.2 nm, YO_5- or YO_7-polyeder with bonds of 0.24 nm, and the BaO_9 or BaO_{10} polyeder with 0.28 nm bond lengths, an unusual shrinkage of the *c*-axis is observed. These structural polyhedrons appear also in other crystals, which have related structures other than the *Pbnm* space group. A modified Vegards rule as described in the next chapter is considered, followed then by the description of the novel method to calculate the dielectric constant from the band structure calculations.

2. Calculation method

The atomic positions according to the space group were taken from[15] and the lattice constant a_0, b_0, c_0 for Y_2BaCuO_5 and their

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substituted materials were either taken from the experimental data[8–10] or estimated from the following ad hoc modified Vegards model: the volume of the unit cell is strongly related to the effective atomic radius (Shannon radius), which ratio is considered in the following formula

$$f_i = \sqrt[3]{\frac{r_i}{r_0}} = \frac{V_i}{V_0} \tag{1}$$

where $r_0 = r_Y$, r_{Ba} or r_{Cu} are the effective cation radii for Y, Ba, Cu and $r_i = r_A$, r_B, r_C those of the substitution elements on the A-, B- or C-site with their coordination numbers 7, 10 and 5. This ratio is in good agreement to the volume expansion. Assuming a fixed shrinkage for the c-axis the a- and b-axes can be calculated from the volume expansion (see results in Table 2):

$$c_i = 0.98\, c_0, \quad \frac{a_i}{a_0} = \frac{V_i}{V_0}, \quad \frac{b_i}{b_0} = \frac{V_i}{(a_i\, c_i)} \tag{2}$$

For the band-structure calculations the ab initio software VASP[22] was used in this study, which is based on the density functional theory (DFT) with optimized pseudo potentials for the electron-ion interaction.[23] The electron wave functions are expanded in terms of the plane-wave set with an energy cut-off of 280 eV with the generalized gradient approximation (GGA) for the exchange and correlation functional.

The dielectric constant was calculated from the following novel method, based on the experience from semiconductor research, that parallel tracking electronic bands lead to a high-k[1]. The area a_i inscribed between two neighboring energy bands $E_i(k)$ was calculated by the following Eq. (1). This value of the area is averaged for the first four pairs of valence bands near the band gap multiplied with their density n_i from the DOS plot:

$$a_{1,2}(E) = \int (E_1(k) - E_2(k))\mathrm{d}k \quad \text{with} \quad E = \frac{1}{2}(E_i + E_j) \tag{3}$$

$$A = \frac{1}{4} \sum_{j=2i \quad \text{with} \quad i=1,2,3,4} a_{i,i+1}(E)\, n_i(E) \tag{4}$$

It was found, that this value of the inscribed area A in between neighboring electronic bands has a linear relationship to the dielectric constant, ε, as described in the following, while areas between lower valence bands or conductions bands are not related. The physical meaning is, that at parallel tracking bands electrons can easily be excited by photons or phonons, independent which k-vector they possess. For prediction of the dielectric constant, ε the results in Fig. 4 were used for correlation to the area A. The band gap was estimated from the density-of-states plot with a special method[24] as it was successfully applied for titania, by assuming a certain threshold value fitted to experimental data.

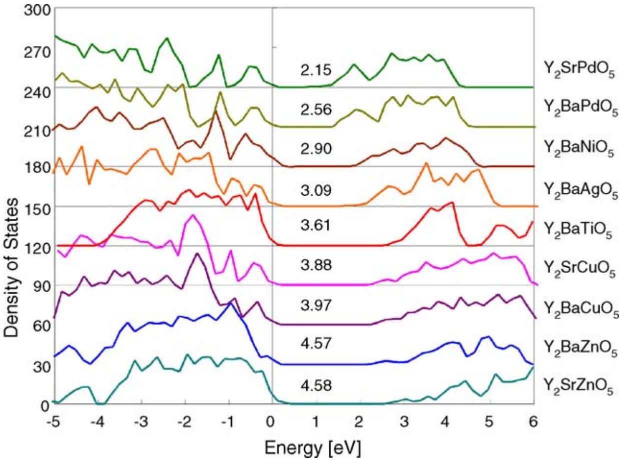

Fig. 1. Calculated Density of states and band gap for the Y2115-substutients considered in this study.

3. Results and discussion

The electronic band structures of Y_2BaAO_5, with A = Cu, Zn, Pd, Ni, Ti, Ag and Y_2SrAO_5, with A = Cu, Zn and Pd were calculated (Table 1). The density of states is shown in Fig. 1 in the order of increasing band gap. The Fermi-Energy was adjusted to zero. The density of states has steep edges on the valence band side for Y_2BaTiO_3, Y_2BaPdO_5 and Y_2SrPdO_5, which would lead to a high effective mass for electron transport. The electronic band structure is shown in Fig. 2 for Y_2BaCuO_5 as a typical example, where for clarification the valence and conduction bands starting from the band gap are marked with V1, V2, V3, V4, ... and C1, C2, C3 and C4. The band structure is drawn from the Γ-point in [0 0 1] to [0 1 1] and [1 1 1] direction, while in Fig. 2(b) from [1 0 0] to [1 1 0]. Compared to the standard drawing for orthorhombic crystals, which considers only the {0 0 1} directions, this modified drawing displays also the [1 1 0] directions and has the advantage that a possible anisotropy, namely a difference in [0 0 1] or [1 0 0] direction can be easily detected. The features of the band structure appear similar for all materials and show a direct band gap and the large amount of parallel bands as typical for materials with high dielectric constant, in particular the pairs V1–V2, V3–V4, V5–V6, V7–V8 are correlated to dielectric constant. The density of states plot in Fig. 2(c) shows, that the bands close to the band gap with their low density contribute only weakly to the properties.

The energy difference between neighboring bands is shown in Fig. 3(a) Y_2BaCuO_5 and (b) for Y_2SrZnO_5. The energy difference is rather large around the Γ-point, while at the X-point (and Y-, Z-points not shown here) it vanishes, according to the degeneration of the bands. When multiplied the integral over these plots with the related density of states, the value of the area A is derived. This shows an good correlation to the experimental value of the dielectric constant as shown in Fig. 4. The four higher valence band pairs (V1–V8) show almost the same correlation $A = 53 \times \varepsilon - 330$, while the correlation of the lower valence bands V11–V10 to ε is not fulfilled. As deduced from this analysis, the high-k material Y_2SrZnO_5 gains its contribution to the dielectric constant mainly from the density of states rather from the parallel bands, which is almost the same for Y_2BaCuO_5 and Y_2SrZnO_5 (Fig. 3).

Table 1
Experimental and calculated data of the microwave properties of Y_2BaCuO_5-based phases

	Experiments				Calculation	
	ε	Q_f (GHz)	τ_f (10^{-6}/K)	References	Band gap, E_g (eV)	Area, A (eV nm^{-4})
Y_2BaCuO_5	9.4	3831	−35.0	8	3.97	234
Y_2BaZnO_5	15.4	113969	−44.5	8	4.57	462
Y_2BaNiO_5[a]	10.1	5834	−35.8	9	2.90	342
Y_2SrCuO_5[b]	12.9	2963	1.6	10	3.88	278
Y_2SrZnO_5[b]	16.7	4920	−35.5	10	4.58	576
Nd_2BaZnO_5	22.6	12451	4.6	11	Not calculated	
Nd_2BaCuO_5[b]	17.6	2205	−18.4	12	Not calculated	
Sm_2BaCuO_5	16.5	53257	−5.2	15	Not calculated	

In the experiment a multiple phase material.

[a] In the experiment the composition was $Y_2Ba(Cu_{0.1}Ni_{0.9})O_5$, because Y_2BaNiO_5 has different crystal structure.

[b] In the experiment the composition was Y_2 $(Sr_{0.7}Ba_{0.3})CuO_5$ and $Y_2(Sr_{0.7}Ba_{0.3})CuO_5$.

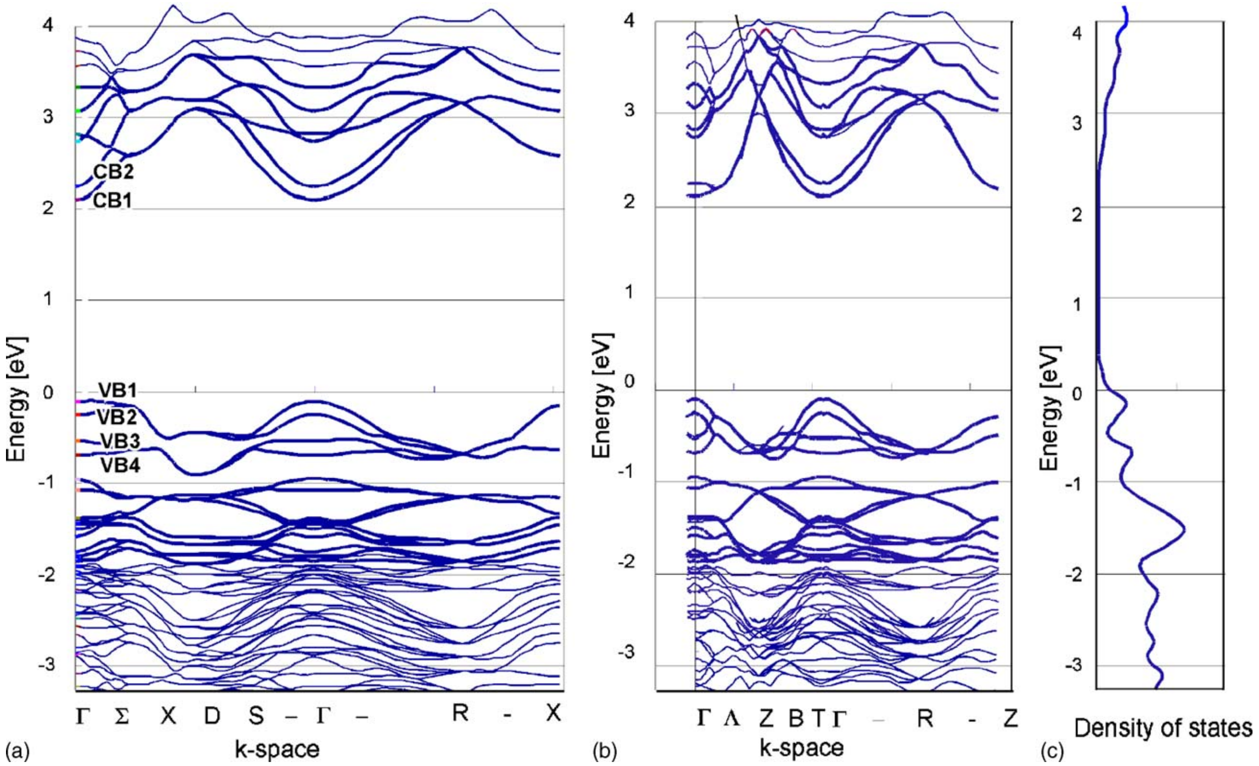

Fig. 2. Electronic band structure of Y_2BaCuO_5, in: (a) [1 0 0]; (b) [0 0 1] direction; and (c) the density of state.

The novel models introduced in this paper for simple calculations of the dielectric constant and the lattice constants could successfully be correlated and predict experimental data. The calculation of the quality factor of the microwave materials requires phonon calculations. Including the expansion and tilting behavior of the three types of coordination polyhedra can improve the reliability of the calculations, also the Vegards rule further. These detailed systematic studies can lead to enhancement of microwave resonance properties and the ab initio simulations presented in this paper are to our best knowledge

Table 2
Prediction of lattice constants and dielectric constants for different substitution in Y_2BaCuO_5

	a (nm)	b (nm)	c (nm)	Band gap, E_g (eV)	Area, A (eV nm^{-4})	ε
Y_2BaPdO_5	1.278	0.578	0.699	2.56	237	10.8
Y_2BaAgO_5	1.448	0.583	0.692	3.09	409	14.2
Y_2BaTiO_5	1.213	0.566	0.706	3.61	383	14.0
Y_2SrPdO_5	1.278	0.568	0.706	2.15	222	11.0

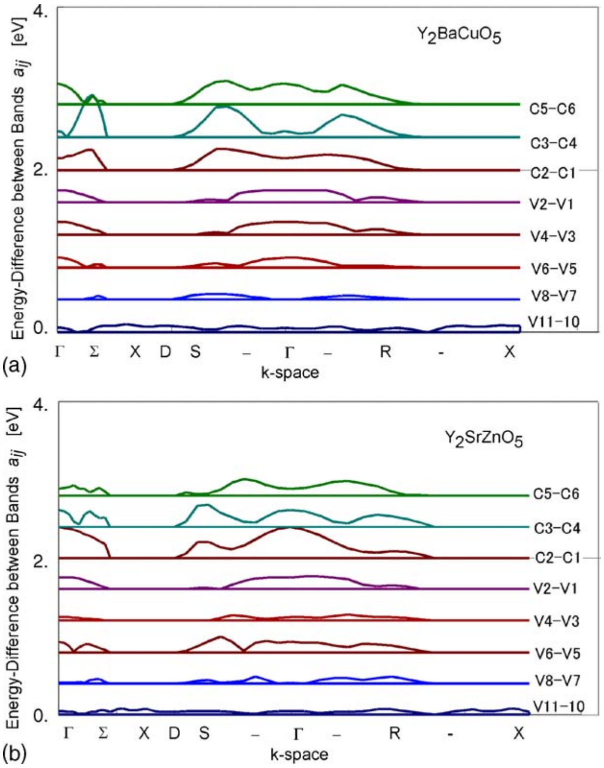

Fig. 3. Energy difference between neighboring bands a_{ij} for the valence and conduction band pairs as marked: (a) Y_2BaCuO_5 and (b) Y_2SrZnO_5.

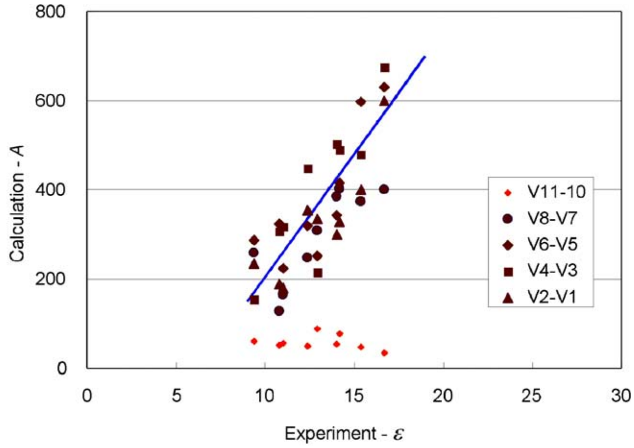

Fig. 4. Correlation between the experimental measured dielectric constant ε and the calculated area A for different energy band pairs as marked.

the first on these materials in order to understand and predict the properties. Calculations of solid solutions or doping are just a matter of computer performance and become more and more feasible.

4. Conclusion

This paper concerns about the improvement of Y_2BaCuO_5-based materials and suggests two novel calculation methods, a modified Vegards rule for estimation of lattice constants and an integration of tracking electronic band difference for estimation of the dielectric constant. The calculation results show a good agreement to the experimental data and predict that Y_2BaAgO_5 and Y_2BaTiO_5 are promising candidates for microwave applications (Table 2).

References

1. Dresselhaus, M.S., Lecture on Solid-State Physics, 1. *Review of Energy Dispersion Relations in Solids*, MIT, Boston, 2001. http://web.mit.edu/afs/athena/course/6/6.732/www/new_part1.pdf, p. 36.
2. Baker, H. J., Hunsche, S. and Kurz, H., *Rev. Mod. Phys.*, 1998, **70**(2), 523–536.
3. Marzari, N. and Singh, D. J., *Phys. Rev. B*, 2000, **62**(19), 12724–12729.
4. Kootstra, F., de Boeji, P. L. and Snijders, J. G., *Phys. Rev. B*, 2000, **62**(11), 7071–7083.
5. Arnaud, B. and Alouri, M., *Phys. Rev. B*, 2001, **63**, 085208.
6. Both, S., Vast, N., Reining, L. and Olevano, V., *Phys. Rev. B*, 2004, **70**, 045301.
7. Parlinski, S., Li, Z. Q. and Kawazoe, Y., *Phys. Rev. Lett.*, 1997, **78**, 4063–4068.
8. Kan, A., Ogawa, H. and Ohsato, H., *J. Eur. Ceram. Soc.*, 2001, **21**, 1699–1704.
9. Kan, A., Ogawa, H. and Ohsato, H., *Mater. Sci. Eng. B*, 2001, **79**, 180–182.
10. Kan, A., Ogawa, H., Ohsato, H. and Ishihara, S., *Jpn. J. Appl. Phys.*, 2000, 5654.
11. Kan, A., Ogawa, H., Ohsato, H. and Ishihara, S., *J. Eur. Ceram. Soc.*, 2001, **21**, 2593–2598, ibid 1731–4.
12. Mori, K., Ogawa, H., Kan, A. and Ohsato, H., *J. Eur. Ceram. Soc.*, 2003, **23**, 2603–2606.
13. Mori, K., Ogawa, H., Kan, A., Ohsato, H. and Ishihara, S., *Mater. Chem. Phys.*, 2003, **79**, 273–275.
14. Mori, K., Ogawa, H., Kan, A. and Ohsato, H., *J. Eur. Ceram. Soc.*, 2004, **24**, 1745–1748.
15. Michel, C. and Raveau, B., *J. Solid State Chem.*, 1982, **43**, 73–80.
16. Rodriguez, C. O., Weiht, R. and Christensen, N. E., *Physica C*, 1997, **282–287**, 1621–1622.
17. Ambrosch-Draxl, C., Blaha, P. and Schwarz, K., *Phys. Rev. B*, 1991, **44**(10), 5141–5147.
18. Ki Hyun Yoon, Eung Soo Kim and Jong Suk Jeon, *J. Eur. Ceram. Soc.*, 2003, **23**, 2391–2396.
19. Cockayne, E., *J. Eur. Ceram. Soc.*, 2003, **23**, 2375–2379.
20. Higuchi, Y. and Tamura, H., *J. Eur. Ceram. Soc.*, 2003, **23**, 2683–2688.
21. Shimada, T., *J. Eur. Ceram. Soc.*, 2003, **23**, 2647–2651.
22. Kresse, G. and Hafner, J., *Phys. Rev. B*, 1993, **47**, 558, ibid 49 (1994) 14251.
23. Kresse, G. and Joubert, J., *Phys. Rev. B*, 1999, **59**, 1758.
24. Wunderlich, W., Miao, L., Tanemura, M., Tanemura, S., Jin, P., Kaneko, K. *et al.*, *Int. J. Nanosci.*, 2004, **3**(4–5), 435–445.