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Contributions to the dielectric constant of the system $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ from packing fraction and nephelauxetic ratio

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An attempt has been made to identify the optimum parameters for good dielectric resonator materials. The dependence of dielectric constant of the system $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ ($\text{Ln}=\text{La}, \text{Pr}, \text{Nd}, \text{Sm}$) on packing fraction and nephelauxetic ratio is discussed. The reported dielectric data for this system were treated using the multiregression method.

I. INTRODUCTION

The present interest in the development of temperature-compensated dielectrics with dielectric constant in the range 70–100 for making dielectric resonators suitable for the lower part of the microwave frequency range makes one look more and more into rare-earth-based systems such as $\text{BaNd}_{2(1-x)}\text{Sm}_{2x}\text{Ti}_5\text{O}_{14}$,¹ $(1-x)(\text{Li}_{1/2}^+\text{Sm}_{1/2}^{3+})\text{TiO}_3-x(\text{Na}_{1/2}^+\text{Sm}_{1/2}^{3+})\text{TiO}_3$,² $\text{BaO-Nd}_2\text{O}_3\text{-TiO}_2$,³ double oxides in the systems $\text{Ln}_2\text{O}_3\text{-TiO}_2$ ($\text{Ln}=\text{La}, \text{Nd}, \text{and Sm}$),⁴ and $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ ($\text{Ln}=\text{Pr}, \text{Nd}, \text{and Sm}$).⁵ Materials for dielectric resonators require high dielectric constant and low dielectric loss with negligible temperature and frequency dependence. The $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ systems having formula units of $\text{Ba}_{3.75}\text{Ln}_{9.5}\text{Ti}_{18}\text{O}_{54}$ with $\text{Ln}=\text{La}, \text{Pr}, \text{Nd}, \text{and Sm}$, has interesting dielectric properties so as to make some of them attractive for dielectric resonator applications. They have distorted perovskite structure with orthorhombic unit cells. The structure and atomic dispositions remain the same as one goes from La to Sm. Even though the changes are only in the kind of Ln^{3+} ion present, which are chemically almost similar, they exhibit appreciable difference in dielectric properties. It is appropriate if one can identify the parameters responsible for this behavior along with their contribution to the dielectric constant. The importance of similar problems has been posed recently by Takahashi and co-workers⁴ and Takahashi *et al.*,² however, they did not report any attempt to quantitatively solve the problem. For this study, the data available (on ceramic pellets without mention of porosity variations) from Mudrolyubova *et al.*⁶ were used for a multiregression analysis and are displayed in Fig. 1.

II. IDENTIFICATION OF PARAMETERS RESPONSIBLE FOR THE CHANGE IN DIELECTRIC PROPERTIES

Two parameters can be identified as responsible for the change in dielectric properties with change in lanthanide ion. One is the ionic radius and the other arises from the nephelauxetic effect. As only the ionic radius of the rare earth ion changes in this system, to adjust with it, the

structure will either expand or contract resulting in a change of packing fraction. With packing fraction the rigidity of the whole system and hence the response with respect to temperature and electric-field intensity and frequency will change as the strength of the phonon modes are affected. Hence, the percentage of packing fraction was taken as one parameter influencing the changes in the dielectric properties of this system.

The packing fraction percent is calculated as follows and the calculated values are given in Table I. The cell volume is taken from Varfolomeev *et al.*⁷ Each of these unit cells contain two formula units of $\text{Ba}_{3.75}\text{Ln}_{9.5}\text{Ti}_{18}\text{O}_{54}$. Ionic radii for all the ions were taken from tables.⁸ The cell volumes were taken from Varfolomeev *et al.*⁷ because Matveeva, Varfolomeev, and Il'yushchenko⁹ have not reported cell parameters and the parameters given by Mudrolyubova *et al.*⁶ and Gens *et al.*¹⁰ are inconsistent with those given by Varfolomeev *et al.*⁷ The data of Varfolomeev *et al.*⁷ are results of continuous iteration of the structural parameters which varied marginally over a period of 10 years. Hence, these latest deductions about the number of formula units, ordering of Ba and Ln ions, and existence of superlattice were considered as the most reliable data for this calculation.

The nephelauxetic effect (reduction in interelectronic repulsion due to complex formation) has a direct bearing on the electronic polarization as it affects $(1-\beta)$, where β is the nephelauxetic ratio which is the ratio of the interelectronic repulsion parameter when the ion is in a complex to that of the free ion.¹¹ The value of $(1-\beta)$ depends both on the central ion and on the surrounding ligands. That is, $(1-\beta)=hk$, where h and k depend on the ligand and the central ion, respectively. In the system considered the ligands also remain the same and hence the changes in the dielectric properties should arise from the k value.

The k values for Pr, Nd, Sm, Gd, and Er were taken from the literature¹¹ and are given in Fig. 2. It has been found that there exists a definite relationship between the k values of these lanthanide (+3) ions and the number of electrons in the 4f shell, namely,

$$k=0.039-0.005f+0.0016f^2. \quad (1)$$

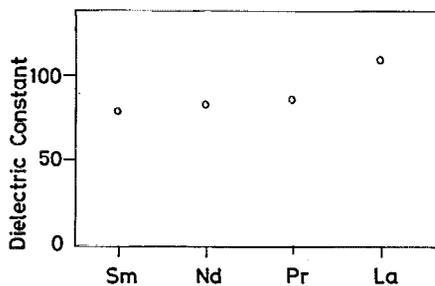


FIG. 1. Dielectric constant of $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ ($\text{Ln}=\text{La, Pr, Nd, Sm}$) compounds at 293 K and 1 MHz frequency (see Ref. 6).

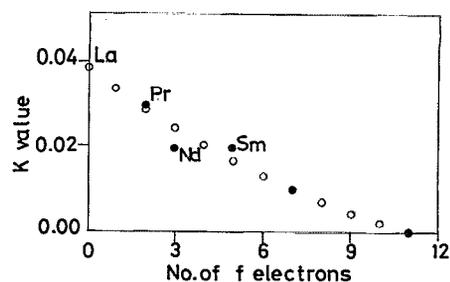


FIG. 2. Variation of k value with the number of f electrons of Ln^{3+} ions. ●: Literature data (see Ref. 7); ○: data fitted to the relation $k=0.039-0.005f+0.00016f^2$.

The k values obtained from this equation are indicated separately in Fig. 2. In Fig. 2 the number of f electrons means the number of $4f$ electrons of the Ln^{3+} ions. The k value for the La^{3+} ion is not reported in the literature and those for other lanthanides are accurate only up to the second decimal place. Hence, the k values for the Ln^{3+} ions were taken from this curve assuming that k values vary smoothly along the rare-earth series as per Eq. (1).

III. CALCULATION TO GET THE FUNCTIONAL RELATIONSHIP BETWEEN PACKING FRACTION, k VALUE, AND ϵ'

To get the functional relationship of k with ϵ' , the data available on the dependence of the h value of ϵ' for halide ligands¹² were taken assuming that both h and k affect the electronic polarization in the same fashion. An exponential function fits the data well (see Fig. 3).

One can see that the packing fraction of the La compound and the Pr compound differ only slightly, still their dielectric data show marked difference. Hence, one has to define a critical packing fraction percent P_c below which the structure loosens to give large dielectric response. The large value of the dielectric constant of this system can be an effect of the value of the packing fraction percent P itself. Therefore, both P and P_c were taken as parameters that influence the dielectric response. The highest packing fraction percent is for the Nd compound (59.19) and was assumed to be the P_c .

A multiregression analysis was carried out using the program EUREKA to get the functional relationship of ϵ' with P and P_c , along with the coefficients of the exponential function which relates the k value with the dielectric constant, and to get the constant part of ϵ' which is inde-

pendent of the lanthanide ion or the rigid lattice contribution to the dielectric constant. EUREKA varies the constants and the coefficients coming in a relation in steps assigned by the user, and gives the total value of ϵ' in each case. The user has to assign the functions and the form of the equation. The program simultaneously varies all the constants and coefficients coming in the equation and keeps calculating the total value of ϵ' . The relationship which gives the set of calculated dielectric constant values for all the lanthanide compounds which match the experimental values are to be accepted. The dielectric constant values at 293 K and 1 MHz were used for this calculation. The condition that various terms must be connected by addition was introduced, because a term coming in subtraction is physically meaningless.

IV. RESULTS AND DISCUSSION

The result of this multiregression analysis gives the equation according to which the dielectric constant of the system $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ varies with respect to the assumed parameters P , P_c , and k . The reason for choosing an exponential function for the dependence of k value on ϵ' is described in Sec. III. Coefficients coming in this dependence and the entire functional dependence of P and P_c on ϵ' are to be found out by the multiregression method. Various combinations of physically realistic functions, coefficients, and constants were tried to arrive at a consistent equation that gives a set of ϵ' values for the four compounds in this system using the respective values of P , P_c , and k . The calculated ϵ' values deviate only slightly from

TABLE I. Values of parameters used in the calculation and the results for the system $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$.

Ln	k	Ionic volume per formula unit \AA^3	Unit-cell volume \AA^3	Packing fraction (PF) (%)	Contribution to ϵ'		Total value of ϵ'	
					k	P.F.	Calculated	Reported
La	0.039	623.97	2134.5	58.46	66.66	31.51	109.36	110.0
Pr	0.029	622.74	2113.2	56.94	54.24	27.43	90.83	87.0
Nd	0.0245	621.53	2100.0	59.19	48.77	26.07	84.0	84.0
Sm	0.017	616.95	2097.2	58.84	40.85	28.11	78.13	80.0

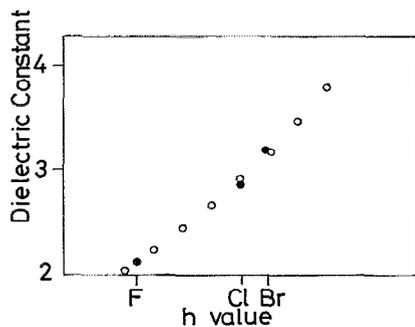


FIG. 3. Increase in the dielectric constant of a system with increasing h value of the halide ligand. ●: Literature data (see Refs. 7 and 8); ○: data fitted to the relation $\epsilon' = 1.72e^{0.26h}$.

the reported ϵ' values as shown in Table I. The relationship obtained for the ϵ' of this system at 293 K and 1 MHz frequency is

$$\epsilon'_i = a \exp(bk_i) + c \exp[d \exp(P_c - P_i)/P_c] + e, \quad (2)$$

with $i = \text{La, Pr, Nd, and Sm}$. The values of each term for the four lanthanide compounds are shown in Fig. 4, and given in Table I. The value of the rigid lattice dielectric constant is approximately 9 as in the case of a tightly packed ionic compound. The component of ϵ' coming from packing fraction shows that ϵ' decreases with increase of P_c of the structure and increases double exponentially with an increase of $(P_c - P_i)$ for a particular compound in the system; but, the contribution from the nephelauxetic effect parameter k is unexpectedly high. If the contribution from k comes only from an enhanced electronic polarization as a result of the expansion of the f or d electron cloud (nephelauxetic effect), its value must be low, since the optical dielectric constant of these materials is only 5.71.⁸ The structure of the $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ system^{7,9} shows that TiO_6 octahedra are held together by lanthanide and barium ions in a little disordered fashion. The only nephelauxetic ion in these compounds are the lanthanide ions. It is possible that the expanded electron cloud of the lanthanide ions could result in increased repulsion between

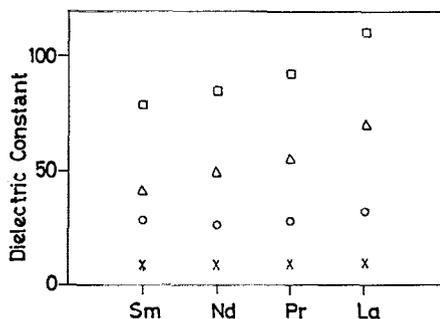


FIG. 4. Components of the dielectric constant of the system $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ as obtained by the multiregression analysis. □ Total value of ϵ' obtained by Eq. (1); Δ contribution from nephelauxetic ratio; \circ contribution from packing fraction; \times constant part common to all compounds in this system.

them, forcing the structure to settle down in an expanded form and giving the TiO_6 octahedra more volume to occupy. In an expanded TiO_6 octahedron the Ti ions will have more freedom to respond to an applied electric field, resulting in an increased value of ϵ' , more so since the Ti ion is highly polarizable and is located at a site where the value of the local Lorentz field factor is higher.¹³ In fact, the structure information given in Matveeva and co-workers⁹ shows that the shortest distance between adjacent rare-earth ions is 36% larger than the shortest distance between neighboring Ba and rare-earth ions. This can be due to increased repulsion between the lanthanide ions or because of the preferential site occupation of barium ions, or by both. The average Ba-O distance is 0.284 nm while the average Ln-O distance is 0.262 nm, as may be expected since the nephelauxetic effect will increase the bonding between the metal ion and the ligand. The distortion in the perovskitelike columns can account for the smaller Ln-O distance while keeping a larger Ln-Ln distance.

The constant coming in Fig. 4, which is indicated by \times in the figure, is the constant value " e " of Eq. (2). This is the value of the dielectric constant which is independent of the two assumed parameters P and k and common to all compounds in the system $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ and its value is 9.165. This can be visualized as the dielectric constant which one would have obtained for this system if k_i values were zero and P_c and P_i values were too large.

The low-temperature dependence of ϵ' of $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$ at 3 MHz given by Poplavko *et al.*¹⁴ was fitted to a seven degree polynomial. The data show that with decreasing temperature below 60 K, the dielectric constant of these compounds first increases and then decreases. The peak is not sharp, but one can identify a particular temperature where ϵ' is maximum, which is designated as the turning temperature T_t . It was found that the same relationship gives the low-temperature dependence of ϵ' of the remaining compounds with a change in the coefficients and T_t . This again implies the correlations existing among various compounds of this system.

V. CONCLUSION

This analysis identifies the electron cloud distribution of the rare-earth ions and the packing fraction of the system as the main parameters responsible for the variation of the dielectric constant in the system $\text{BaLn}_2\text{Ti}_4\text{O}_{12}$. The result of this work implies that to get a good dielectric resonator material, (a) the large metal ions which support the basic building blocks (in this case TiO_6 octahedra) should be able to offer a wider cage to the basic building block so that it will be also able to respond to electric fields through the presence of a highly polarizable ion at the center of the building block where the local Lorentz field factor is high; (b) P_c of the system should have an optimum value, because too large a P_c value will give a very low ϵ' and too small a P_c value will give a large value of ϵ' with temperature dependence; and (c) within one system, ions that give an optimum $(P_c - P_i)$ value must be chosen. $(P_c - P_i)$ is the difference in packing fraction of a particular

compound in the system with respect to the critical packing fraction P_c . This quantity needs to have an optimum value to make the material useful for application in dielectric resonators (DR), because a DR needs high ϵ' with low ϵ'' and temperature-independent characteristics. Equation (2) shows that as $(P_c - P_i)$ decreases, value of ϵ' decrease; but, if $(P_c - P_i)$ increases, ϵ' will increase, but generally ϵ'' and temperature dependence also will increase. Hence, one has to choose the particular compound in a system having an optimum $(P_c - P_i)$ value which will give all the required characteristics of a DR.

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