

Dielectric relaxation in sillenite crystals $\text{Bi}_{12}\text{SiO}_{20}:\text{Fe}$

Castro R A ¹, Nabiullina L A ¹, Shadrin E B ²

1 Herzen State Pedagogical University of Russia,
Saint Petersburg, Russia.

2 Ioffe Physical-technical Institute of Russia Academy of Sciences,
Saint Petersburg, Russia.

e-mail: lia-nabiullina@yandex.ru

Abstract

Within the range of low frequency and temperature between 293 and 373 K, temperature-frequency dependences of the dielectric permittivity and losses in iron-alloyed $\text{Bi}_{12}\text{SiO}_{20}$ crystal are investigated. Introduction of impurities into the crystal structure leads to greatest losses and change of the dielectric constant. The results are being discussed involving the concept of formation of the “impurity-vacancy”-type quasi dipoles with iron, resulting from the substitution of M-cations by Fe^{3+} ions at the centers of oxygen tetrahedra.

1. Introduction

Sillenite crystals of $\text{Bi}_{12}\text{SiO}_{20}$ (BSO) have body-centered cubic lattice of symmorphic space group $I23 (T^3)$ [1]. Currently more than 60 compounds like sillenite $\text{Bi}_2\text{O}_3\text{M}_x\text{O}_y$ with cations M^{n+} were synthesized, as well as their numerous solid solutions. Alloying of Fe sillenites is of particular interest [2], because ferrum (as well as chrome) is always present in these compounds as background impurity. Increased value of dielectric capacitance, minor losses and thermal stability make them advanced / perspective materials for microwave technology [3]. In particular, sillenite crystals doped with ferrum are successfully used as optical stoppers for eye protection or protection of light sensors in photosensitive devices against blinding effect of laser radiation of visible range.

The objective of this work is analysis of peculiarities of dielectric relaxation processes in BSO crystals: undoped crystals, as well as ones doped with ferrum ions, by means of analysis of their dielectric characteristics at applied field's temperature and frequency variation.



2. Experiment procedure

In this experiment, there were used samples of bismuth silicate grown by Czochralski method. Doping with ferrum ions was carried out at the synthesis stage by means of adding iron trioxide Fe_2O_3 into original load. Doping concentration of Fe was defined according to transmission spectrum and EPR [4]. The samples were prepared in form of discs with diameter 20.0 mm and thickness 1.0 mm. For electrical measurements a layer of silver paste was applied on both sides to provide secure contact. Doping concentration of ferrum ions was approximately $1,7 \cdot 10^{16} \text{ cm}^{-3}$.

Measurements of dielectric parameters were carried out in frequency range of $10^{-2} \div 10^4$ Hz and interval range from 293 to 473 K by means of a spectrometer «Concept-41» made by Novocontrol Technologies GmbH company. Voltage delivered to the sample was 1.0 B, temperature stabilization accuracy was $\pm 0,3^\circ\text{C}$. Electrical quantity measurement error did not exceed 5%.

3. Results and discussion

According to figure 1, dielectric capacitance ϵ' drops dramatically with frequency increase, its significant reduction starts from 0,01 Hz up to 10 kHz for all chosen temperatures. Maximum value of ϵ' can be clearly observed at frequency 0,01 Hz for all analyzed temperatures. Thus, ϵ' depends heavily on temperature in low frequency range. High value of dielectric capacitance at low frequency in the crystals under study is probably associated with cavities, dislocations and other defects [7], as well as with participation of interfacial polarization [6, 8].

Figure 2, showing the temperature dependence ϵ' , demonstrates that ϵ' is constantly rising at all frequencies. Although, maximum value of ϵ' turned out to be at 473 K for all analyzed frequencies. With temperature rise, the polarizability is rising at the expense of lattice defects development [5], which can be seen in increase of dielectric capacitance with increase of temperature. In this search sharp increase of ϵ' with temperature at all frequencies analyzed here can also be associated with polarization of space charge [6].

Figure 3 shows frequency dependence of dielectric dissipation factor, and this dependence demonstrates that the parameter is considerably reducing with increase of frequency from the first measurement to frequency of 10 Hz. In this frequency range, $\tan\delta$ depend heavily on frequency, after which they slightly decrease with the increase of frequency to the value of 10 kHz, at which saturation phase comes, i.e. $\tan\delta$ depend slightly on frequency in high frequency range.

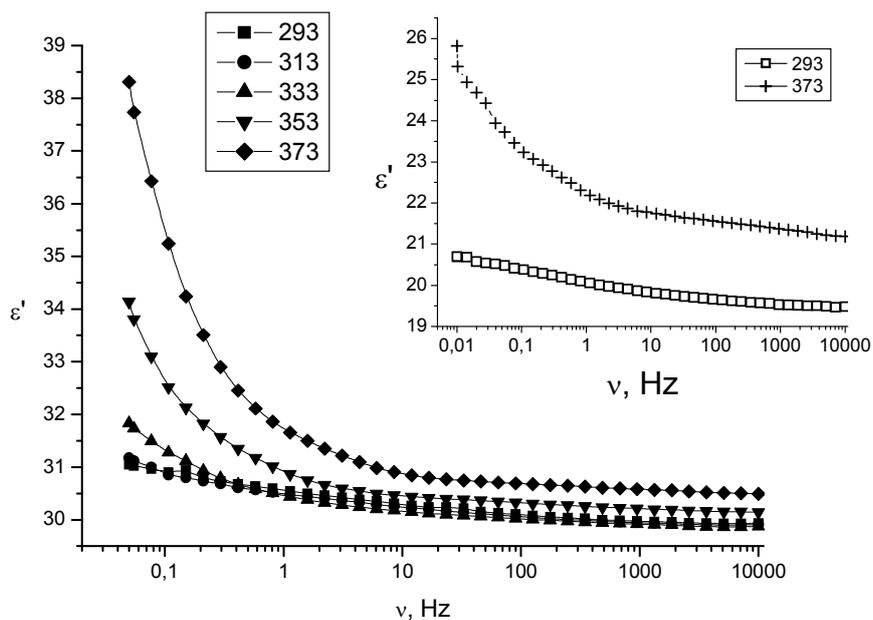


Figure 1. Frequency dependence of dielectric capacitance at following temperatures: 313, 353, 393, 433, 473 K.

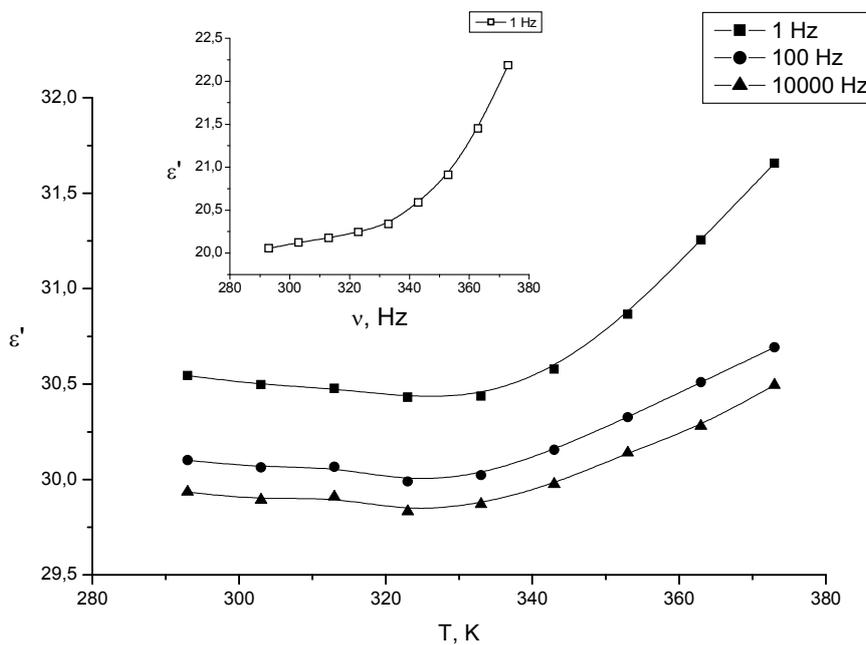


Figure 2. Temperature dependence of dielectric capacitance at following frequencies: 10^0 , 10^2 , 10^4 Hz.

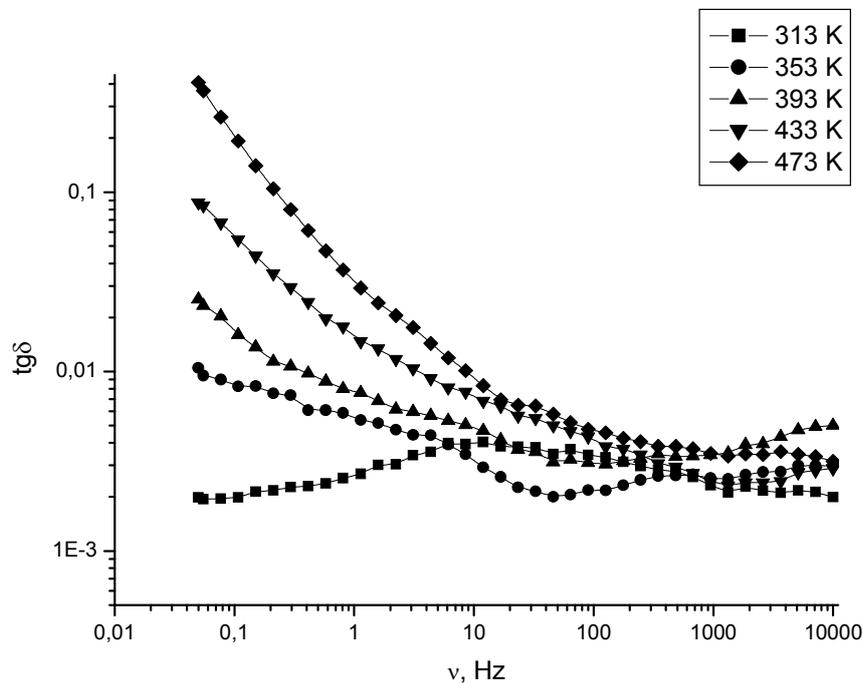


Figure 3. Frequency dependence of dielectric dissipation factor at following temperatures: 313, 353, 393, 433, 473 K.

Frequency dependence of complex dielectric capacitance ε'' imaginary part of BSO samples is shown in Figure 4. Discovered maximum losses at room temperature suggest that there is relaxation process of non-Debye type. Existence of non-Debye type relaxation process is confirmed during parameter estimate in two-parameter empiric function of Havrilyak-Negami (HN) [9]:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau)^{\alpha_{HN}}\right]^{\beta_{HN}}} \quad (2)$$

where ε_{∞} - high frequency limit of dielectric capacitance's real part, $\Delta\varepsilon$ – dielectric increment (difference between low frequency and high frequency limits), $\omega=2\pi f$, α_{HN} and β_{HN} – form parameters, describing symmetrical ($\beta=1$ – Cole-Cole model) and asymmetrical ($\alpha=1$ – Cole –Davidson model) expansion of relaxation function [9]. Values of the parameters are shown in Table 1.

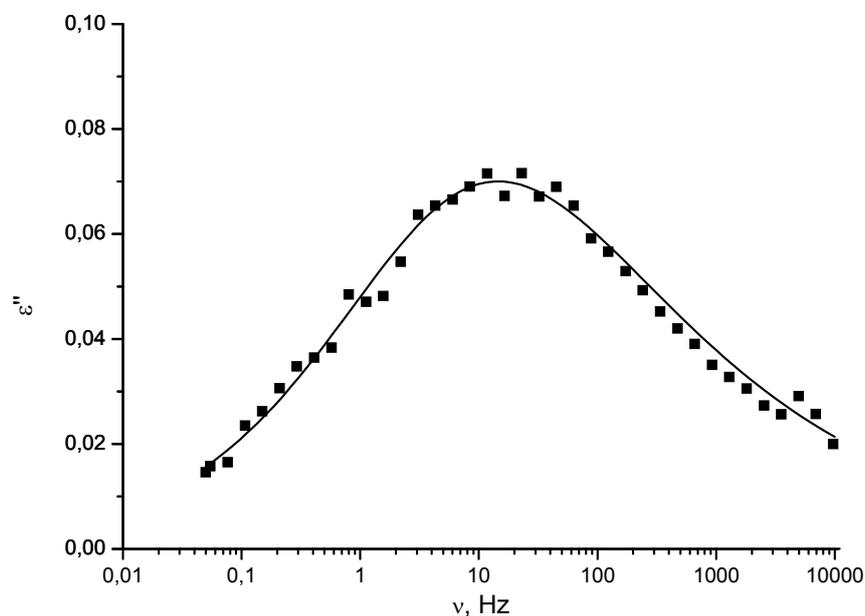


Figure. 4. Frequency dependence of imaginary part of dielectric capacitance at 293 K. Dots indicate experimental values, full line shows theoretical curve.

Table 1. Value of relaxation parameters according to Havrilyak-Negami approximation

τ_{\max} [s]	$\Delta\epsilon$	τ , s	ϵ_{∞}	α	β	Temp. [K]	AC Volt [Vrms]
0.01	0.43	0.03	1.0000	0.50	0.55	293	1.0000

The look of Cole-Cole diagram (figure 5) also indicates a wide spectrum of relaxation times in the sillenite crystals under study, caused by structural defects and presence of ferrum impurity. Quasidipoles of “impurity-vacancy” type with participation of ferrum can be relaxation oscillators. They appear if Fe^{3+} ions replace M-cations in the centers of oxygen tetrahedrons; and in one of the sites there should be an oxygen vacancy that captured an electron (according to charge compensation).

Migrations of this vacancy in the area of multiwell potential of oxygen tetrahedrons cause participation of quasidipoles in thermal orientation of polarization.

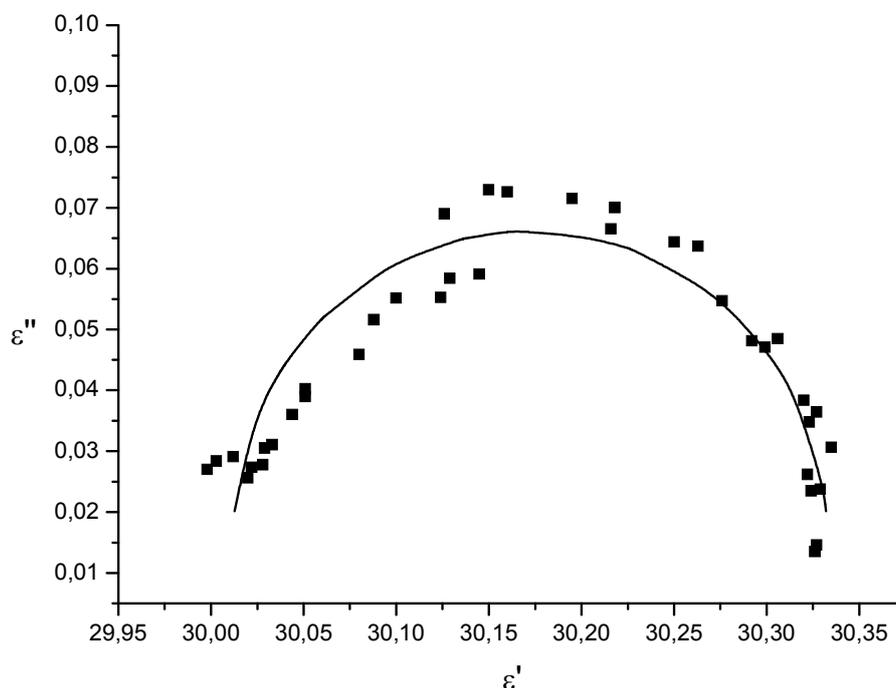


Figure. 5. Cole-Cole Diagram for T = 293 K.

4. Conclusion

Introduction of Iron impurity into the structure of sillenite crystals causes maximum losses and excursion of dielectric capacitance. The look of Cole-Cole diagram for alloy samples indicates a wide spectrum of relaxation times in the crystals under study, caused by structural defects and presence of ferrum impurity.

References

- [1] Yu Hu and Derek C Sinclair 2013 Relaxor-like Dielectric Behavior in Stoichiometric Sillenite $\text{Bi}_{12}\text{SiO}_{20}$ *Chemistry of materials* **25** pp 48-54
- [2] Briat B Grachev V G Malovichko G I Schirmer O F and Wohlecke M 2007 Defects in Inorganic Photorefractive Materials and Their Investigations *Photorefractive Materials and Their Applications* Springer Series in Optical Sciences **114** pp 9-49
- [3] Nabiullina L A Shadrin E B 2012 Magnetic resonance properties of single crystals $\text{Bi}_{12}\text{SiO}_{20}:\text{Fe}$ *Izvestia: Herzen University Journal of Humanities & Sciences* **147** pp 63-72
- [4] Panchenko T V Karpova L M Duda V M 2000 Dielectric relaxation in $\text{Bi}_{12}\text{SiO}_{20}:\text{Cr}$ crystals *Physics of the Solid State* **42** 4 pp 689-693
- [5] Amarendra Singh K Goel T C and Mendiratta R G 2002 Dielectric Properties of Mn-substituted Ni-Zn Ferrites *Journal of Applied Physics* **91** 10 pp 6626-6629
- [6] Lal B Khosa S K Tickoo R Bamzai K K and Kotru P N 2004 Dielectric Characteristics of Melt Grown Doped KMgF_3 Crystals *Materials Chemistry and Physics* **83** pp 158-168

- [7] Sirdeshmukh L Krishna Kumar K Laxaman S B Krishna A R and Sathaiah G 1998 Dielectric Properties and Electrical Conduction in Yttrium Iron Garnet (YIG) *Bulletin of Materials Science* **21** p 219
- [8] Mahajan R P Patankar K K Kothale M B and Patil S A 2000 Conductivity, Dielectric Behaviour and Magneto-Electric Effect in Copper Ferrite-Barium Titanate Composites *Bulletin of Materials Science* **23** p 273
- [9] Kremer K Schonhals A (Eds.) 2003 Broadband dielectric spectroscopy *Springer* Berlin Heidelberg p 729