Rev.Adv.Mater.Sci. 12 (2006) 150-153

A CORRELATION BETWEEN EPR AND DIELECTRIC STUDIES FOR LBO DOPED WITH MANGANESE

I.E. Lipiński[1], J. Kuriata[1], N.A. Korynevskii[2] and M. Soboń[3]

[1] Institute of Physics, Szczecin University of Technology, Aleja Piastów 17, 71-310 Szczecin, Poland
[2] Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland
[3] The Faculty of Management and Economics of Szczecin, University of Szczecin, 71-004 Szczecin, Poland

Received: November 12, 2005

Abstract. The temperature dependence of the EPR spectrum of lithium tetraborate ($Li_2B_4O_7$) single crystal doped with manganese is presented. Taking into account thermal expansion (contraction) and spin-phonon effects, two anomalous regions of the temperature behaviour were found: one beginning at about 270K and the other at about 365K. This anomalous behaviour seems to correlate very well with the literature data on the results of dielectric measurements. It is suggested that such anomalous behaviour can be adequately interpreted in terms of the so-called modified two-sublattice model of Mitsui in which both short- and long-range interactions of BO_4 groups are simultaneously included in the Hamiltonian describing the system.

1. INTRODUCTION

Interesting physical properties of LiB_4O_7 (lithium tetraborate called further as LBO) were reported in many papers (see, for example [1,2]). Also, a variety of experimental methods were applied to study material but, as far as we know, magnetic resonance methods have been so far used only to measure the components of ^{7}Li and ^{11}B nuclear quadrupole interaction with the conclusion that no anomalous behaviour is observed in the temperature range from 80 to 300K. Below we present our temperature dependence EPR measurements of LiB_4O_7 doped with manganese. Preliminary data were already presented during the RAMIS conferences [3,4].

Because some details of the crystal structure of LBO will be used in the part of the paper devoted to theoretical considerations, we briefly quote below the data given in [5-7].

The crystal has the space group $I4_1cd$ (or C_{4V}). The unit cell is tetragonal with the dimensions a=0.9477 and c=1.0286 nm. The unit cell contains eight molecules, which are located at body-centered positions. A part of the crystal structure seen along the c-axis is shown in Fig. 1a.

It is worth noting that in the crystal structure one can clearly distinguish two inequivalent BO_4 tetrahedra, which are linked by sharing common oxygen and form a part of the B_2O_7 group. The arrangement of BO_4 tetrahedra is shown in Fig. 1b.

Corresponding author: E. Lipinski, e-mail: Eryk.Lipinski@ps.pl

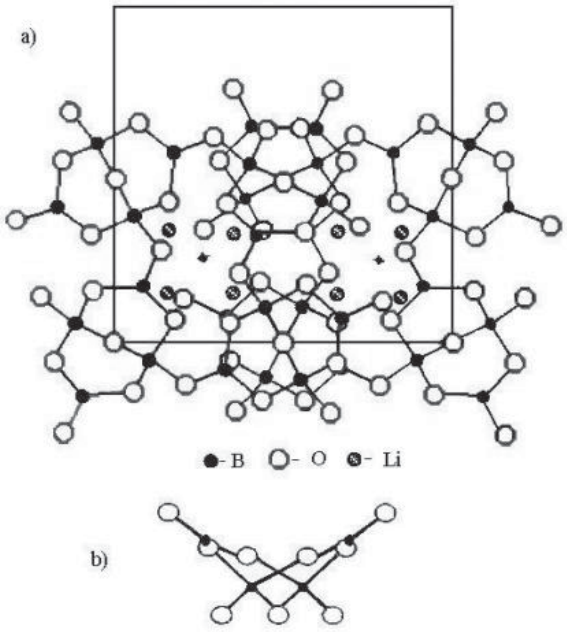

Fig. 1. (a) The crystal structure of LBO seen along the *c*-axis. (b) Basic building blocks of BO_4 tetahedra seen along *a*-axis.

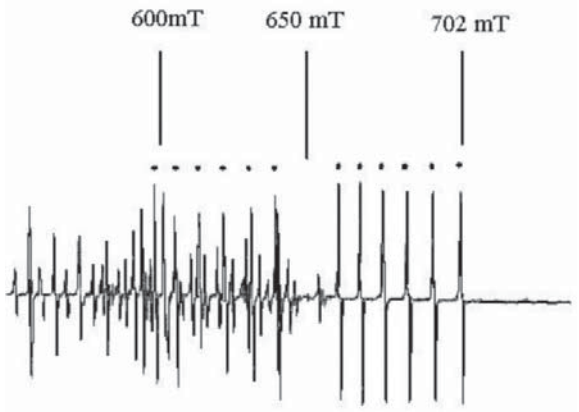

Fig. 2. High magnetic field portion of the EPR spectrum of manganese doped LBO recorded at room temperature with the magnetic field along one of principal direction.

Finally, reporting the literature data useful for this paper we, should add that LBO is ferroelectric with T_c=720K [8] and the Debye temperature resulting from heat measurements is θ_D=302K [9].

The aim of this paper is to report the temperature dependence of the high magnetic field part of the EPR spectrum of manganese doped LBO, to compare it with the data of dielectric measurements, to suggest a theory, which could account for the detected anomalies, and finally, to determine the values of the principal parameters appearing in the suggested model.

2. EXPERIMENTAL

Large and transparent single crystals of LBO with clearly formed crystals faces were grown by the modified Bridgman method in the Department of Physics, Uzhgorod National University. The nominal concentration of the dopant (manganese ions) was estimated to be about 0.1 mol.%.

Two standard X-band EPR spectrometers working with 100 KHz modulation of a steady magnetic field were used. For the temperature range from 300K down to 30K we used a Bruker E-500 spectrometer with an Oxford Instruments Cryostate and for higher temperature measurement we used a Radiopan spectrometer with a home-made heater. In this latter case, two thermoresistors placed just above and below the crystal sample were used to stabilize the temperature estimated to be not worse than ±5K.

3. RESULTS AND DISCUSSION

A high magnetic field portion of the EPR spectrum of manganese doped LBO is shown in Fig. 2. The temperature dependence of the EPR line position was measured for different high field hyperfine lines and an example is shown in Fig. 3 for the extreme lying line.

Dielectric measurements of pure LBO were reported by Maeda *et al.* [1]. In particular, the temperature dependence of the dielectric susceptibility was measured in the temperature range from about 10K up to 870K. The dielectric susceptibility does not change with the temperature from about 10K up to about 270K. However, a rapid growth in ε was detected above ~270K. Above 300K, many anomalies in the behaviour of $\varepsilon(T)$ were observed, among which there was one appearing at about 365K.

Comparing these data with the results of our EPR measurements, a strict correlation between EPR and dielectric measurements seems to be very probable. Additional indication of the above supposition is the fact that above 270K we observed also a clear

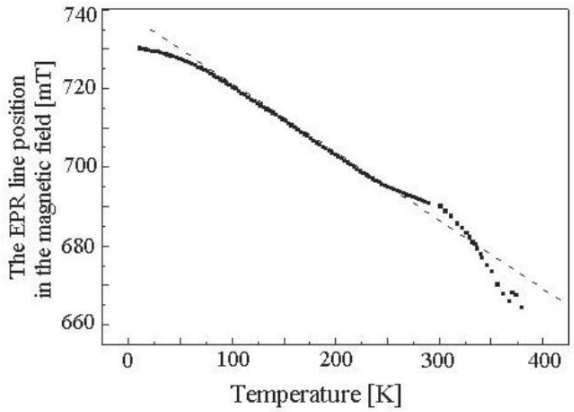

Fig. 3. Temperature dependence of the EPR line position measured at 9.4 GHz in the magnetic field for the extreme line.

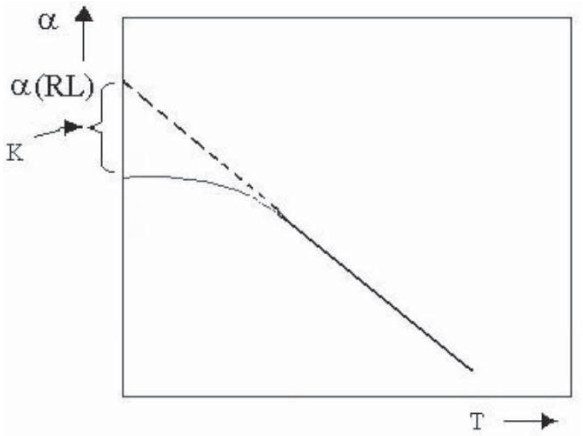

Fig. 4. General temperature dependence of the α spin-Hamiltonian parameter resulting from Eq. (1).

decrease in the EPR line intensity being consistent with the increase of the dielectric susceptibility of the material studied.

In most general terms, the zero field splitting (ZFS) can be described by a set of spin-Hamiltonian parameter α. Their temperature dependence can be expressed by the following relation:

$$\alpha = \alpha_0 + aT + [\text{phonon contribution}]. \qquad (1)$$

Here: the first term describes the so-called rigid lattice contribution, the second term includes the effect of thermal expansion, and the third term is determined by the assumed model for spin-phonon interaction.

Since spin-Hamiltonian parameters should be related to the internal energy of the system, they can be parameterised according to any model for crystal lattice vibrations known so far. There exist three such approaches called as: the Einstein, Debye, and Huang models. The first two models are well known and need not to be discussed here. Huang model can be understood as a sort of a compromise between them. In this model, we deal with vibrations of quantum harmonic oscillators modulated by lattice waves; so, the phonon contribution is given by [10]:

$$\alpha(\text{phonon}) = K\left[1 + 4\left(\frac{T}{\theta_D}\right)^2 \int_0^{2\theta_D/T} \frac{x}{e^x - 1}\,dx\right]. \qquad (2)$$

Independently of the assumed model, the temperature dependence of the α-parameter has approximately the run shown in Fig.4.

In previous reports, e. g. [11] it was found out that the temperature dependence of the α-parameter should be linear above ~77K

$$\alpha = \alpha_0 + AT. \qquad (3)$$

Any deviation from this dependence should be carefully examined as it may indicate the existence of some anomalies mainly connected with phase transitions taking place in the system. In our case, see Fig. 3, we observe two clear deviations above 77K: one appearing at about 270K and another one at about 365K. In the temperature range from 10 to 225K, the temperature dependence of the EPR line position can be very well described using the Huang parameterisation scheme yielding us the following best fit parameters: α_0=740mT, K=10.5 mT, and θ_D=253K.

3. THEORETICAL CONSIDERATIONS

Because of some specific particularities of the crystal structure of LBO (two coupled BO_4 active groups) and our previous experience in studying the systems in which rotations of two active groups were involved in ferroelectric phase transitions and anomalous behaviour of dielectric susceptibility, polarization, and specific heat, we are inclined to adopt here

the model we carefully tested on SASD type crystals [12,13].

The model is principally based on the assumption that considering simultaneously short- and long-range interaction between active groups, one can obtain, within the frames of the so-called two-sublattice model of Mitsui, two order parameters describing the system: one is the obvious polarization *P* and the other new, denoted by ξ, is a parameter characterising an antiferroelectric coupling between active groups in the same cell.

The form of the Hamiltonian is given in [13]. This form leads, after rather tedious calculations, to an explicit expression for free energy *F* for such systems. Analyzing this expression, we have got a system of two equations determining not only *T*c, but also other temperature points in which one should expect the appearance of some anomalies. This set of equations is:

$$\begin{aligned} & 1+e^{\frac{\beta_c K}{2}}\,\mathrm{ch}\frac{\beta_c}{2}\left[(\tilde{J}-\tilde{K})\xi_c+2\Delta\right] \\ & -\frac{\beta_c}{2}\frac{\left(\tilde{J}+\tilde{K}+\delta\right)^2}{\tilde{J}+\tilde{K}}=0, \\ & \xi_c\left[1+e^{\frac{\beta_c K}{2}}\,\mathrm{ch}\frac{\beta_c}{2}\left[(\tilde{J}-\tilde{K})\xi_c+2\Delta\right]\right] \\ & -e^{\frac{\beta_c K}{2}}\,\mathrm{sh}\frac{\beta_c}{2}\left[(\tilde{J}-\tilde{K})\xi_c+2\Delta\right]=0. \end{aligned} \qquad (4)$$

Here: $\tilde{J}$ is a parameter describing interactions of active groups belonging to same sublatice, $\tilde{K}$ is a parameter describing interactions of active groups belonging to different sublatices , Δ is an asymmetrical parameter of Mitsui and δ describes non-equivalence of rotations of active groups below T_c.

Detailed computer simulations of Eq. (4) were carried out with the conclusion that two anomalous regions observed both in EPR and dielectric measurements can be very well accounted for accepting that $\tilde{J}$=1330K, $\tilde{K}$=-410K, Δ=5K, and δ=2.5K.

3. CONCLUSIONS

1. Temperature dependence of the EPR spectrum of LBO detected at temperature below 270K can be parametrized using either Einstein, Debye, or Huang model.

2. The model of Huang seems to be, however, most effective because the Debye temperature determined from this scheme of parametrization is most close to that determined from heat measurements.

3. EPR measurements proved to be in good correlation with dielectric measurements in detecting the temperature regions in which some anomalies are observed.

4. Theoretical analysis within the so-called modified two-sublattice model was used to analyse the obtained experimental results.

REFERENCES

[1] M. Maeda, H. Tachi, K. Honda and I. Suzuki // *Jpn. J. Appl. Phys*.**33** (1994) 1965.
[2] Y.M. Ivanov, Ya.W. Buriak and K.S. Aleksandrov // *Solid State Phys*. **32** (1990) 11.
[3] D. Podgórska, J. Kuriata, I.E. Lipiński, V. Rizak and M. Krupski, In: *Proc. of the RAMIS 2003 Conf.*, Institute of Molecular Physics, Polish Academy of Scienses (Poznań, 2003) P-20.
[4] I.E. Lipiński, J. Kuriata, V.M. Rizak, N.A. Korynevskii and M. Soboń, In: *Proc. of the RAMIS 2003 Conf.*, Institute of Molecular Physics, Polish Academy of Scienses (Poznań, 2005) P-24.
[5] Krogh-Moe // *Acta Cristollogr*. **15** (1962) 62.
[6] Krogh-Moe // *Acta Cristollogr*. **B24** (1968) 179.
[7] M. Natarajan, F. Faggiani and I.D. Brown // *Cryst. Struct. Commun.* **8** (1979) 367.
[8] J.W.Cha and J.M.Kim // *Ferroelectrics* **197** (1997) 93.
[9] H.A.A. Sidek, G.A. Saunders and B. James // *J. Phys. Chem. Solids* **51** (1990) 457.
[10] C.Y. Huang // *Phys. Rev.* **159** (1967) 683.
[11] F.J. Owens, In: *Magnetic Resonance of Phase Transitions*, ed. by F.J. Owens, C.P. Poole and H.A. Farach (Academic Press: New York, San Francisco, London, 1979) 297.
[12] J. Kuriata, I.E. Lipiński, N.A., Korynevskii and T. Bodziony // *Physica* **B307** (2001) 203.
[13] I.E. Lipiński, N.A. Korynevskii, J. Kuriata and W. Pastusiak // Physica **B327** (2003) 116.