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Magnetic relaxation in $Zn(PO_3)_2 \cdot Er(PO_3)_3$ glass

M. Orendáč [a,*], K. Tibenská [b], E. Čižmár [a], V. Tkáč [a], A. Orendáčová [a], J. Holubová [c], Z. Černošek [a,b,c], E. Černošková [c]

[a] Institute of Physics, P.J. Šafárik University, Park Angelinum 9, 041 54 Košice, Slovak Republic
[b] Faculty of Aeronautics, Technical University, Rampová 7, 041 21 Košice, Slovak Republic
[c] University of Pardubice, Faculty of Chemical Technology, Department of General and Inorganic Chemistry, Studentská 573, Pardubice 53210, Czech Republic

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ABSTRACT

The results of experimental studies of alternating (ac) magnetic susceptibility and specific heat of $Zn(PO_3)_2 \cdot Er(PO_3)_3$ glass are reported. Despite a high concentration of magnetic Er(III) ions the analysis of ac susceptibility ruled out the formation of a spin glass state in the used range of temperatures. Two relaxation processes were identified. The first one is thermally activated with a crossover in its temperature dependence observed at nominally 7 K. The relaxation at lower temperatures seems to be governed by a direct process with pronounced effect of phonon bottleneck. Striking deceleration of spin dynamics with increasing temperature found above 7 K is tentatively attributed to overcoming Ioffe – Regel crossover and strong scattering of acoustic phonons on local modes. Simplified prediction derived from a soft-mode-dynamics model confirms the presence of the boson peak observed in specific heat data and reasonably predicts the temperature of the crossover. The second process is consistent with a cross – tunneling relaxation. The obtained results suggest that magnetic doping of glasses and studying magnetic relaxation may represent an alternative tool for the investigation of lattice modes in glasses.

1. Introduction

The structures of glasses lack any translational symmetry and the absence of long-range order in the glassy network may lead to physical properties significantly different from those found in regular crystalline solids. One of the notable features of glassy materials is an excess of vibrational density of states in the terahertz frequency range, the density being higher that that predicted by the Debye theory. The low – temperature broad anomaly in specific heat, which appears in Cp/T^3 vs. T dependence, is believed to be a consequence of the excess vibrational density of the states. This so - called "boson peak" is also manifested as a broad band in Raman spectra and neutron scattering data at low energies [1]. The fact, that the boson peak was found in various organic, inorganic and metallic glasses suggests that it represents a universal feature of amorphous matter. Although the close relation of the boson peak to transverse acoustic phonons has been clarified yet, its physical origin is still under discussion. More specifically, it was theoretically proposed that the boson peak in glasses corresponds to acoustic van Hove singularity in crystals [2], suggesting that the boson peak may originate merely from acoustic phonons. However, different approaches suggest a dominant role of localized vibrational modes associated with long-lived locally favored structures [3], or predict the existence of the crossover between acoustic waves and local modes [4].

Scattering of the acoustic phonons in the quasi local vibrations and their relation to the boson peak was theoretically investigated in [5,6]. Furthermore, the relationship between the quasi-local vibrations, the boson peaks and the van Hove singularities was analyzed in [7]. The concept of fractals has also been adopted leading to the suggestion of a phonon - fracton crossover in glasses [8]. Experimental studies of cesium borate confirmed the absence of the influence of the composition on the position of the boson peak, indicating a localized nature of the vibrations responsible for the excess specific heat [9]. Systematic studies of binary lithium borate glasses revealed that the excess heat capacities are scalable to a single master curve and the relation of the boson peak to the excess vibrational density of states was supported [10]. In addition, the crossover from phonon to fracton excitations was proposed by specific heat and thermal conductivity measurements of silica aerogels at low temperatures [11].

It has been argued, that the decision about the true scenario may not be straightforward, since the available experimental data may be interpreted using various different theoretical models, thus the origin of the boson peak has not been reliably explained yet [2]. The extension of the investigated quantities might represent an alternative way towards an unambiguous choice of the adequate theoretical model. More specifically, apart from specific

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[*] Corresponding author.

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heat, neutron scattering and Raman spectroscopy, also the investigation of the magnetic relaxation in magnetically diluted glasses might be instructive. The properties of magnetic ions embedded in a glassy matrix have been intensively studied, however, to the best of our knowledge, the interest has been focused on their optical properties [12–14].

Given that for each relaxation process the energy levels of a magnetic ion and appropriate frequencies of phonons are important, the investigation of the magnetic relaxation will determine not only a type of the relaxation process, but may also give insight in the nature of the lattice excitations involved in the relaxation. The aforementioned motivation stimulated our interest in the experimental study of magnetic relaxation in $Zn(PO_3)_2 \cdot Er(PO_3)_3$ glass at temperatures, where a spin - glass state is not formed yet. In this temperature range, the relaxation of a single spin to phonon bath should dominate. If the relaxation is to be governed by a single relaxation process, then any observed anomaly in the temperature dependence of the relaxation time may be related to specific properties of the available phonon modes.

2. Experimental details

The studied $Zn(PO_3)_2 \cdot Er(PO_3)_3$ and $Zn(PO_3)_2$ glasses were prepared by melt-quenching method. The appropriate amounts of ZnO, Er_2O_3 (both 99.9%; Sigma-Aldrich), and H_3PO_4 (85%, p.a.; Sigma-Aldrich) were mixed in a platinum crucible. Using an electric furnace the mixture was heated slowly up to 600 °C for approximately 4 h and then heated to 1200 °C and melted for 10 min at this temperature. The molten material was quenched by pouring on a graphite mold preheated to approx. 250 °C to minimize the internal stress of glass and the prepared glasses was subsequently slowly cooled to room temperature. Powder X-ray diffractometer D8 Advance (Bruker), CuK(α) radiation, was used to confirm the amorphous state of glasses. Raman spectra were measured by confocal Raman microscope LabRam HR (Horiba Jobin Yvon) using 633 nm excitation laser and objective 10 ×, 20 scans of 5 s exposition were collected for each spectrum.

Studied glasses belong to the group of phosphate-based glasses with a glassy network consisting of tetrahedral phosphate units. These tetrahedral units are linked through covalent bridging oxygens and are classified using Q^n terminology, where n represents the number of bridging oxygens per tetrahedron [15]. Depending on the value of n there could exists four different structural units: Q^3 forming three - dimensional cross-linked network (vitreous P_2O_5 or ultraphosphate glasses); Q^2 units typical for metaphosphate glasses with polymer-like structure; Q^1 units terminating chains and Q° units forming discrete orthophosphate species.

The $Zn(PO_3)_2$ and $Zn(PO_3)_2 \cdot Er(PO_3)_3$ glasses should have the metaphosphate composition, so it can be supposed that their structure consists mainly of Q^2 structural units forming both chain or ring type arrangements. The chains of various length are terminated by pyrophosphate units Q^1, [16]. The Zn(II) ions were found to be coordinated by four oxygens [17] and Er atoms selectively coordinate to the terminal oxygen of P=O site [18].

Thermomechanical measurements were performed using TMA Q400EM (TA Instruments). For ac susceptibility measurements single piece of $Zn(PO_3)_2 \cdot Er(PO_3)_3$ glass of 14.6 mg weight was placed into a plastic holder, which was held by a straw. The ac susceptibility measurements were performed in a commercial SQUID magnetometer MPMS Quantum Design. Calorimetric studies were conducted using pieces of $Zn(PO_3)_2 \cdot Er(PO_3)_3$ and $Zn(PO_3)_2$ glasses with 3.5 and 4.2 mg weight, respectively. The specific heat of both glasses was studied using a relaxation technique in a commercial system PPMS Quantum Design.

3. Results and discussion

The Raman spectra of $Zn(PO_3)_2$ and $Zn(PO_3)_2 \cdot Er(PO_3)_3$ glasses show band at 700 cm^{-1} assigned to the symmetric stretching of bridging oxygens connecting the neighboring Q^2 structural units and band close to 1200 cm^{-1} of the symmetric stretching of non-bridging oxygen in Q^2 units, typical pattern of metaphosphate composition [10], see Fig. 1.

Selective coordination of Er to the terminal oxygen of P=O site causes strengthness of the structure reflected by dramatic increase of the glass transformation temperature from 426 °C to 576 °C for $Zn(PO_3)_2$ and $Zn(PO_3)_2 \cdot Er(PO_3)_3$, respectively, and simultaneous decrease of the thermal expansion coefficient from 6.98 to 5.17 μm/(m K).

Temperature dependence of the alternating susceptibility was investigated from 2 K to 15 K at the frequencies from 0.1 Hz to 1 kHz and magnetic fields 0.5 T, 1 T, 1.5 T, 2.5 T. It should be noted, that in zero magnetic fields no sensitivity to excitation frequency was found. The real and imaginary components of the susceptibility studied at 1.5 T for selected frequencies are presented in Fig. 2a and b, respectively. Similar behavior was found for other magnetic fields. More specifically, the real component, χ', is characterized by a round maximum, which tends to be less pronounced and for increasing frequency is shifted towards higher temperatures. More complicated behavior was found in the imaginary component, χ''. This quantity displays a pronounced maximum, which at very low frequencies rapidly grows with increasing frequency and then it is suppressed slightly moving towards higher temperatures. The sensitivity of the position of the maxima of both χ' and χ'' to the temperature suggests thermally activated relaxation. Presumably random positions of magnetic Er (III) ions in a glassy matrix may lead to a suggestion that a spin – glass state can be formed in $Zn(PO_3)_2 \cdot Er(PO_3)_3$. Indeed, if the approach from Ref. [19] is adopted and the temperature dependence of the relaxation time is constructed from the maxima of the real component in the ac susceptibility, its low – temperature part can be analyzed using a theory for dynamical scaling near a phase transition

$$\tau = \tau_0 \left(\frac{T_f}{T_f - T_c} \right)^{zv}. \tag{1}$$

Here, T_f is the frequency – dependent freezing temperature determined by the maximum in ac susceptibility, zv is dynamic exponent, τ_0 represents a characteristic relaxation time and T_c is a

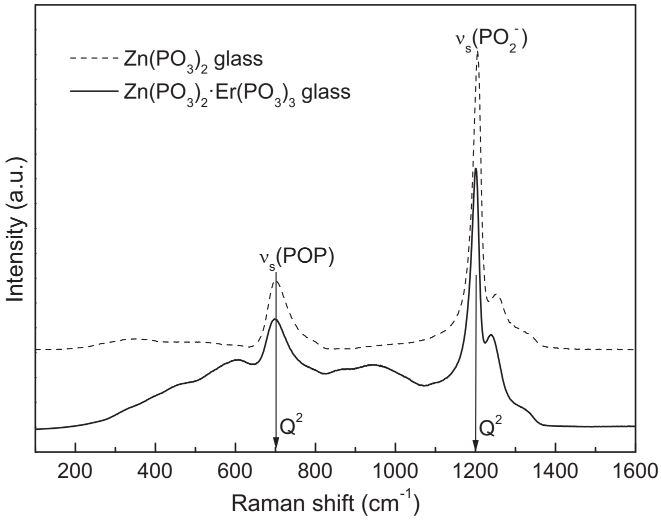

Fig. 1. The Raman spectra of $Zn(PO_3)_2$ and $Zn(PO_3)_2 \cdot Er(PO_3)_3$ glasses.