Research Article

Preludes to the Lattice Compatibility Theory LCT: Urbach Tailing Controversial Behavior in Some Nanocompounds

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We try to give an explanation to the unexpected Urbach tailing associated to some phenomena which occur in some nano-compounds lattices. The provided discussion and notes are detailed here as a prelude to the lattice compatibility theory (LCT), a guide to a plausible understanding of this unsolved intrigue.

1. Introduction

Urbach tailing alterations inside nanostructured lattices (Figure 1) have been always attributed to atomic-scale topological disorder, unexpected hybrid excitonic transitions, or topological filament occurrence [1–4]. In the beginning of the last decade, Urbach tailing has been attributed to the hydrogen content, and precisely the different E_{04} and sp^2 contents inside nanofilms [5]. Another more realistic explanation has been provided earlier by Dow and Redfield [6]. This explanation claims that Urbach tailing is due to the broadening of the exciton absorption band which occurs when charged impurities in the lattice induce phonon-induced microelectric fields. This phenomenon has been also described, in II–VI compound semiconductors, as a reduction of holes-electrons Coulombic interactions which results in more free excitons, as long as exciton radii are larger than those of alkali halides. Many other causes have been proposed in the relevant literature [7–10].

In this paper, a prelude to the micro-chemistry-related Lattice Compatibility Theory (LCT) is provided as an attempt to explain Urbach tailing alterations in nano-structured lattices. The study is organized as follows. In Section 2, the experimental details and motivations are presented along with the studied nanomaterials patterns. In Section 3, the fundamentals of the proposed Lattice Compatibility Theory LCT are discussed. Last section is a conclusion which summarizes the aim methods and perspectives of the work.

2. Experimental Details and Motivations

In this study, targeted nano-materials are some bismuth oxides BSO, BGO, and BTO. These nano-materials are technologically interesting material, because they can function as a Pockels readout optical modulation (PROM) device and photorefractive sensors [11–18]. Crystals of these oxides were grown from highly purified Bi_2O_3 , SiO_2 and presintered BGO, and BTO powders using the Czochralski technique [19]. Elaboration was carried out in room atmosphere and the growing temperature was about 1110°C . Doped nanocrystals were prepared with doping content of 0.02 mol.% in the starting melt and the samples were reexcited each optically by UV radiations for photochromic effect studies.

In order to understand Urbach tailing alteration following doping agent insertion in host structures, Urbach energy E_u has been determined, for doped and undoped samples through the equations:

$$\begin{aligned} \text{Ln}(\alpha(h\nu)) &= \text{Ln}(\alpha_0) + \frac{h\nu}{E_u}, \\ E_u &= \alpha(h\nu) \left(\frac{d[\alpha(h\nu)]}{d[h\nu]} \right)^{-1} = h \left[\frac{d}{d\nu} (\text{Ln}\alpha(\nu)) \right]^{-1}, \end{aligned} \quad (1)$$

where $\alpha(h\nu)$ represents, for each sample, the experimentally deduced optical absorption profile.

FIGURE 1: Urbach tails occurrence scheme.

TABLE 1: Values of Urbach energy for doped and undoped nanofilms.

Nanofilm		E_U (meV)
BSO	Un-doped	842.4
	Doped	304.5
BTO	Un-doped	564.6
	Doped	559.2
BGO	Un-doped	448.7
	Doped	430.5

The width of the localized states (band tail energy or Urbach energy E_u) has been estimated (Table 1) from the slopes of the plots of $(\ln \alpha(\nu))$ versus energy $h\nu$.

3. Results and Discussion

As stated earlier, the Lattice Compatibility Theory LCT refers to the behavior of the doping element intrinsic lattice inside the hosting edifice. In the actual situation, the location of holes in both doping agent oxide, BSO, BTO, and BGO lattice structures along with the nature of the highest occupied band, is determinant in conventional orbitals patterns-linked geometry framework. In this context, some relevant observations have been recorded. The first concerns annealing process which led to the creation of an important number of nonparamagnetic new centers. The induced change seems to cause reduction of both oxygen and bismuth. This reduction has been associated with strong changes in the magnitude of the photosensitivity and the dark and hence less stability.

The second is that despite having the same structures as BSO, nano-structured BGO and BTO react differently under doping. In fact, according to the results recorded in Table 1, the important decrease of Urbach energy with doping ($\approx 60\%$) reveals an increasing order that occurs in well-crystallized doped bismuth sillenite BSO contrasts unexpectedly the un-doped ones. This change is absent in the case of doped BTO and BGO. As it was postulated that Urbach energy is a material parameter which indicates the shape of transition from the band tail to the mid gap states (Figure 1), a possible cause to this difference can be attributed to the disposition of the doping agent inside the host matrices (Figure 2(a)). In a first possible scheme, CuO_2 copper metallic original fcc lattice is incorporated as such inside BSO host matrix (Figure 2(b)). The second scheme is based on the particularities of CuO_2 bonding direction $(\pi, 0)/(0, \pi)$. It is known CuO_2 layers are simply stacked in fourfold symmetry, without other atoms in the crystal. Bond lengths comparison has been favorable to possible adoption to two adjacent O atoms from tetragonal bismuth as edges of CuO_2 lattices (Figure 2(c)). Finally, a possible scheme is based on the magnetic properties of the Cu_2O_3 spin lattices (Figure 2(d)). In this case, a consolidated stabilization inside the host structure is implemented by symmetrically sharing B–O bands hexagonal bonds. This stability has been recorded by Troth and Dainty [20]. These searchers confirmed in their studies on holographic interferometry and anisotropic self-diffraction in sillenite nano-materials that Cu–O bounds in Cu_2O_3 edifices are mainly caused by $3d^9$ configuration of the doping agent ion in a tetrahedral field [20]. On the other hand, it has been confirmed [21–25] that BGO and BTO present distorted octahedral the bismuth-oxygen coordination made

FIGURE 2: Polyhedra structure in BSO matrix. (a): Un-doped, (b): CuO doped, (c): Cu₂O₂ doped, and (d): Cu₂O₃ doped.

up by five oxygen atom and a lone-pair playing the role of the sixth anion. The actually presented Lattice Compatibility Theory (LCT) features are in good agreement with the precedent analyses as well as the notions of lone-pair orbitals, misfit dislocation, and critical layer thickness [26–30]. The disparity and the introduced uncertainty are recorded for BSO, BTO, and BGO nano-materials plea in favor of this theory as long as it explains the lattice compatibility, the interfacial potential energy, and the strain-associated structural accommodation which were monitored exclusively in the case of BSO.

4. Conclusion

In this work we have tried to give a prelude to the Lattice Compatibility Theory (LCT) as an explanative guide for understanding Urbach tailing features inside some nano-materials. The stability of doping agents in host matrices has been the main fundament to this theory, as it was recorded exclusively in some particular lattices. In order to implement thoroughbred fundamentals to this theory, it is necessary to investigate the growth kinetics of differently doped oxides in terms of interaction between host matrix and doping agents' intrinsic structures.

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