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Characteristics of the optical absorption edge and defect structures of La^{3+} -doped PbWO_4 crystals

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Abstract

The UV optical absorption edge of pure PbWO_4 (PWO) and a series of La^{3+} -doped PbWO_4 crystals was measured at room temperature. Parameters, including the energy gap E_g and the energy of phonon E_p involved in the indirect transition, were calculated, and the dependence of the transition on impurities instead of phonons in heavily doped PWO:La crystals is presented. The shift of the absorption edge to higher energy observed in the case of doping at low concentration (<400 ppm) and the red-shift of the cut-off edge found for doping at higher concentration (>1600 ppm) are explained by the combined effects of ion polarization and localized defect energy level. FT-IR spectra of the WO_4 tetrahedron confirmed the coexistence of interstitial oxygen and Pb vacancies to keep the charge balance in heavily doped PWO:La crystals.

1. Introduction

Since the approval of lead tungstate single crystals, PbWO_4 (PWO), as a part of the scintillation detector system for the Large Hadron Collider in CERN, PWO has been extensively studied to improve the radiation hardness of the crystals and to identify possible defect structures in PWO and related crystals due to its merits of high density, short radiation length and fast decay time [1, 2]. Such defects, which may result from non-stoichiometric crystal growth or may be produced by radiation during use, can exert a significant influence on the scintillation performance of this material.

It has been well established that radiation hardness and transmittance of PWO crystals can be effectively enhanced by annealing in air at high temperature [3, 4] and/or by doping with some aliovalent ions [5, 6].

Considering the radius and electronegativity, trivalent positive rare earth ions, such as La^{3+} and Y^{3+} , are believed to substitute for Pb^{2+} and induce an excess positive charge in the PWO host [4, 7], which is compensated by V_{Pb} through the formation of defect complexes

[$2RE_{Pb}-V_{Pb}$] [8]. Investigations of PWO crystals annealed in air have elucidated that interstitial oxygen could also contribute to the defect structures under suitable conditions [7, 9, 10]. On the other hand, the behaviours and correlation of defect structures, including V_{Pb} , V_O , O_i and Re_{Pb} , are still an open question despite many efforts having been made.

Recently, Itoh *et al* [11] reported that the absorption spectra of PWO crystals obey the Urbach rule except for low temperature ($T < 100$ K) when an intrinsic absorption band at 3.5 eV was taken into account, and they supposed that it is the existence of the 3.5 eV band that results in the deviation of the actual absorption tail from Urbach law.

In the present paper, we try to calculate the indirect transition optical parameters of pure and La^{3+} -doped PWO crystals, and study the shift of the absorption edge with increasing La^{3+} content in the PWO host, by which means the change of defect structures is discussed. The selection of PWO:La crystals is based on the following facts:

- (1) La at low concentration leads to dramatic improvements in the transmission in the wavelength range of 330–450 nm [5], which can let us obtain a real absorption edge.
- (2) With a further increase in La^{3+} concentration, different effects appear [12].

This implies a transformation of the doping mechanism, which can help to acquire knowledge of the defects. To derive more detailed information on the defect transformation, FT-IR spectra of the WO_4 tetrahedron are exploited.

2. Experimental details

Undoped PWO and a series of La^{3+} -doped PWO single crystals were grown by the Czochralski method from 5N powders in stoichiometric ratio. The PWO crystals grown were transparent, colourless and crack-free. The concentration of La^{3+} was 100, 200, 400, 1600 ppm, 2.0 and 8.0 mol% for PWO:La crystals, respectively. The sample doped with La^{3+} at 8.0 mol% was grown by the same method at Furdkawa Co. Japan. All samples were cut from grown crystals with dimensions of $10 \times 10 \times 1$ mm³ and their orientations were confirmed by x-ray analysis. Both large facets were polished. Taking account of the anisotropy, crystals with their large faces perpendicular to both the a -axis (A-face) and to the c -axis (C-face), were prepared in our experiments. Samples for IR measurement were also made from the single crystals by grinding them into fine powders, and pressing with KBr into plates.

The optical transmittance of the samples was recorded with unpolarized light using a Shimadzu UV-2501 spectrophotometer at room temperature, the accuracy of which achieved ± 0.002 abs. Fourier transform infrared (FT-IR) spectra of the powder PWO:La samples and Raman spectra of crystal samples were all collected on a Digilab-FTS-80 spectrophotometer.

3. Results and discussions

Absorption coefficients were determined based on the Mclean formula:

$$T = \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \quad (1)$$

where α is the absorption coefficient, T the transmittance, d the crystal thickness in centimetres, and R the reflectance. R can be calculated by

$$R = \frac{(n - 1)^2}{(n + 1)^2} \quad (2)$$

where n is the refractive index. We fitted the results of Baccaro's work by using a Cauchy equation to obtain the dependence of n on the wavelength [13]. The absorption spectra of

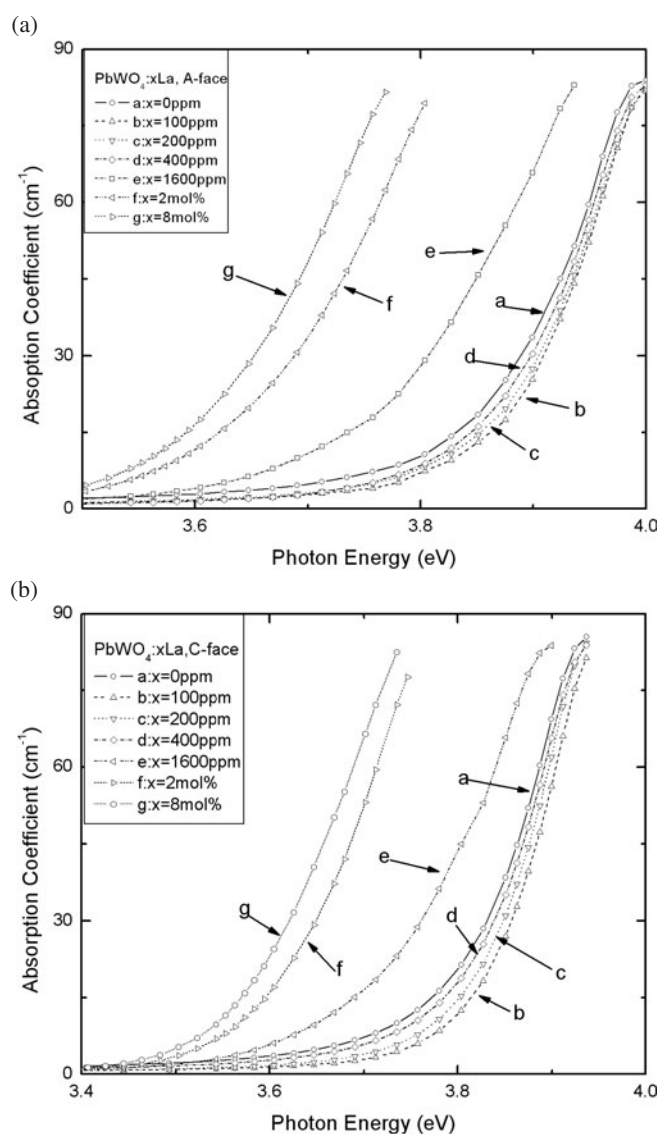


Figure 1. Optical absorption spectra of PWO:xLa ($x = 0, 100, 200, 400, 1600$ ppm and 2, 8 mol%), (a) for A-face samples, (b) for C-face samples.

PWO and PWO:La crystals in the cut-off edge region are shown in figure 1. The absorption band at 3.5 eV was strongly suppressed in PWO:La samples compared to that of pure PWO.

In figures 1(a) and (b), the same change law was found for both A-face samples and C-face samples. For simplicity, C-face crystals are used as examples for the following discussion.

In general, the optical absorption edge of a crystalline solid consists of two energy regions. In the low energy area, α is proportional to $\exp(h\nu)$, while in the high energy field, α obeys the following relationship [14]:

$$(\alpha h\nu) \propto (h\nu - E_g)^m \quad (3)$$

Table 1. The E_g and E_p values of pure and La^{3+} -doped PWO crystals.

| PbWO ₄ :xLa | A-face | | C-face | |
|------------------------|-----------------|---------------------------|-----------------|---------------------------|
| | E_g (eV) | E_p (cm ⁻¹) | E_g (eV) | E_p (cm ⁻¹) |
| $x = 0$ ppm | 3.69 ± 0.01 | 258 ± 16 | 3.65 ± 0.01 | 274 ± 16 |
| $x = 100$ ppm | 3.75 ± 0.01 | 258 ± 16 | 3.71 ± 0.01 | 250 ± 16 |
| $x = 200$ ppm | 3.72 ± 0.01 | 242 ± 16 | 3.69 ± 0.01 | 258 ± 16 |
| $x = 400$ ppm | 3.71 ± 0.01 | 258 ± 16 | 3.68 ± 0.01 | 266 ± 16 |
| $x = 1600$ ppm | 3.53 ± 0.01 | — | 3.51 ± 0.01 | — |
| $x = 2$ mol% | 3.45 ± 0.01 | — | 3.43 ± 0.01 | — |
| $x = 8$ mol% | 3.43 ± 0.01 | — | 3.42 ± 0.01 | — |

where E_g is the optical energy gap, $m = 1/2$ for direct transition and $m = 2$ for indirect transition.

In the indirect transition, momentum conservation can be satisfied by phonon cooperation or impurity scattering. In pure and lightly doped materials, phonon absorption and emission are the overwhelming means for conserving momentum. On the other hand, if impurity scattering conserves momentum, which may occur in degenerate materials, no phonon is involved and the photon energy truly represents the separation between the initial and final states. PWO is an indirect gap material [15]. The absorption coefficient α relationship to the energy close to fundamental absorption edge can be expressed as [16]:

$$\alpha = F(N)\{A_a[h\nu - (E_g - E_p)]^2 + A_e[h\nu - (E_g + E_p)]^2\} \quad (4)$$

where $F(N)$ is a constant dependent on the impurity concentration N , E_p is the energy of the phonon participating in the indirect transition, and the two constants, A_a and A_e at room temperature, are nearly independent of $h\nu$. The first term on the right-hand side of equation (4) represents a transition with phonon absorption, whereas the second term corresponds to phonon emission.

$\alpha^{1/2}$ is plotted as a function of incident energy $h\nu$ for undoped and La^{3+} -doped PWO crystals in figures 2(a) and (b), in which the scattered symbols represent experimental results and the solid lines are fits to equation (4).

The two branches corresponding to phonon emission and absorption in higher energy field are clearly observed in figure 2(a) for all curves. By fitting to equation (4), the values of E_g and E_p at room temperature were determined, and they are listed in table 1. However, figure 2(b) shows that only one straight line appeared in the higher energy field for heavily doped PWO:xLa ($x = 1600$ ppm, 2 and 8 mol%) samples, which implies that impurities rather than phonons play the key role in the process of indirect transition. In this case, the absorption coefficient depends on the concentration of dopant, and it can be determined by

$$\alpha = F(N)A(h\nu - E_g)^2. \quad (5)$$

The fitted results are also included in table 1.

The energies of phonon were estimated ranging from 242 to 274 cm⁻¹. The Raman spectra in figure 3 of these samples show little change of phonon energies with increasing content of La^{3+} . Jayaraman *et al* [17] have seen ten frequencies in the case of PWO: they are 59, 67, 80, 93, 182, 329, 360, 755, 769, 908 cm⁻¹, respectively. It is reasonable to conclude that the present values of phonons are due to the average value of these phonon energies.

Figure 4 shows the La^{3+} doping concentration dependence of the indirect transition energy E_g . It is clear that with the increase of La^{3+} content in the crystals, the alteration of absorption edges can be grouped into two stages. The violet-shift of the absorption edge can be seen in the

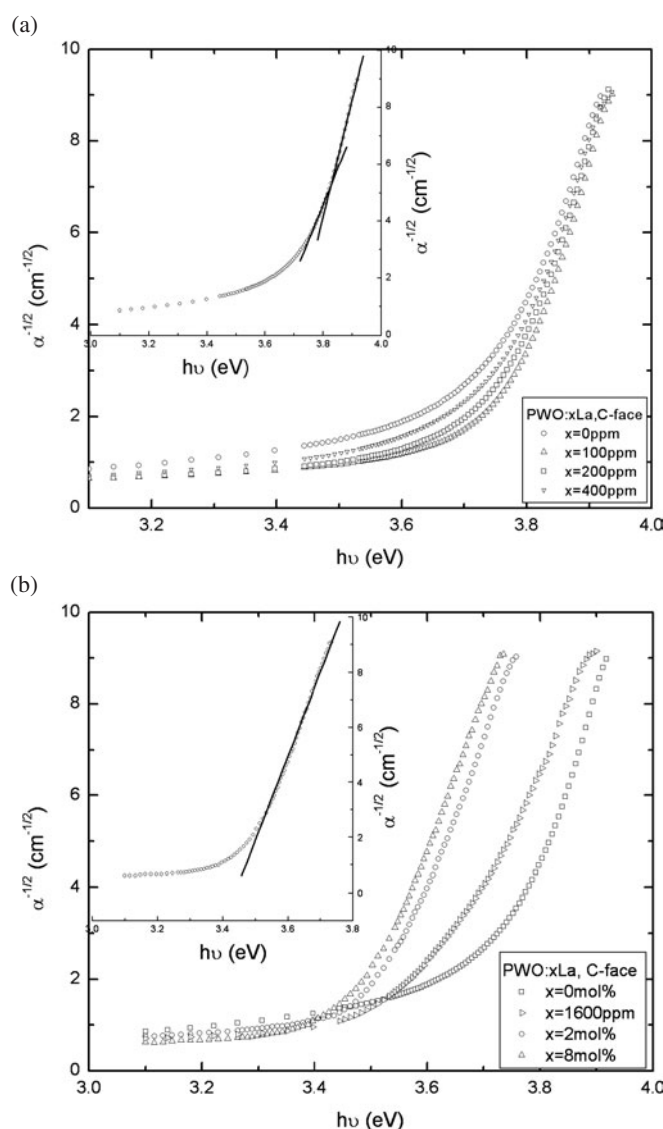


Figure 2. $\alpha^{1/2}$ versus the photon energy ($E = h\nu$) of PWO:*x*La single crystals (C-face) (a) $x = 0, 100, 200,$ and 400 ppm (b) $x = 0, 1600$ ppm, 2 and 8 mol%. In the inset, a least-squares fit (solid line) is illustrated.

case of PWO:*x*La ($x = 100, 200, 400$ ppm) compared to the pure PWO sample. In contrast, the absorption edges move towards lower energy when the added La³⁺ content is more than 1600 ppm. The highest value of the band gap energy is found in the crystal containing 100 ppm La³⁺, and then the band gap energies decrease with increasing amount of La³⁺.

The absorption edge of PWO crystals is caused by the transition from the O(2p) ground state to the W(5d) excited state [15]. Therefore, the change of the distribution of the O²⁻ ion electron will directly affect the forbidden band gap. In the first stage, the displacement of the indirect transition absorption edge of doped La³⁺ crystals may be interpreted by using the ion-polarization model [18]. The polarizability of cations is reflected by $(Z^*)^2/r$ [19], where

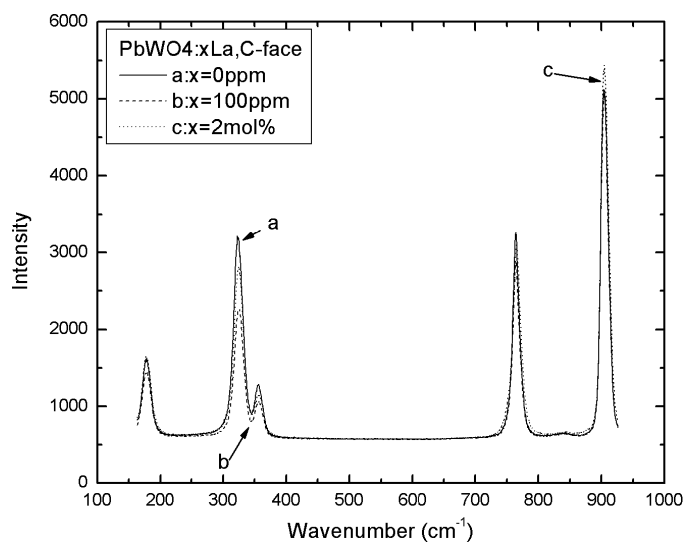


Figure 3. Raman scattering spectra of the $\text{PWO}:x\text{La}$ single crystals ($x = 0, 100$ ppm and 8 mol%, C-face)

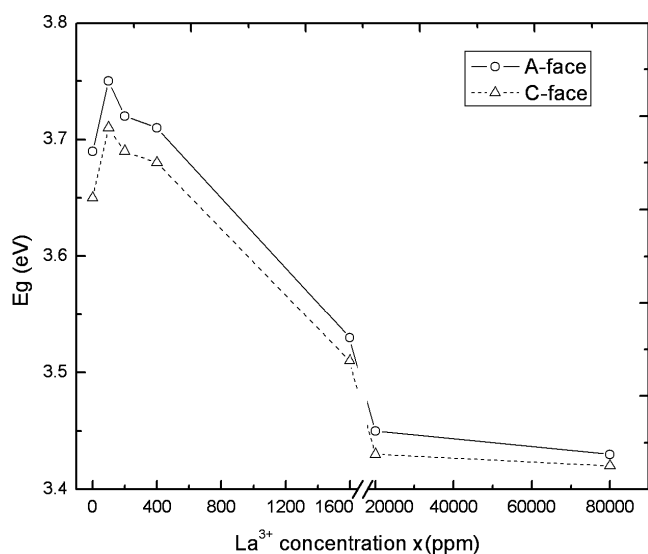


Figure 4. The optical band gap E_g of $\text{PWO}:x\text{La}$ as a function of the La^{3+} concentration x at room temperature.

Z^* is the effective nuclear charge and r is the radius of the ions. Z^* can be expressed by the formula $Z^* = (Z - \sigma)$, in which Z is the nuclear charge of the cations, and the constant σ is a measure of the screening effect on a given electron by all the other electrons present. The values of $(Z^*)^2/r$ of La^{3+} , Pb^{2+} , and W^{6+} are given in table 2.

Because the polarizability of La^{3+} is less than that of Pb^{2+} , the substitution of La^{3+} into the Pb^{2+} site in the lattice will make the polarization of O^{2-} decrease and thereby the energy of an electron transition from $\text{O}(2p)$ ground state to $\text{W}(5d)$ excited state will enlarge, which

Table 2. The values of Z^{*2}/r of La³⁺, Pb²⁺ and W⁶⁺. (Z —atomic number; Z^* —effective nuclear charges, obtained by using Slater's rule; r —the radius of the ions.)

| Ion | La ³⁺ | Pb ²⁺ | W ⁶⁺ |
|------------|------------------|------------------|-----------------|
| Z | 57 | 82 | 74 |
| Z^* | 4.2 | 4.5 | 7.2 |
| r (nm) | 0.116 | 0.120 | 0.063 |
| Z^{*2}/r | 15.2 | 16.9 | 82.3 |

causes the indirect transition absorption edge to move towards violet. On the other hand, calculation and experiment [20, 21] have suggested that both Pb vacancies (V_{Pb}) and La_{Pb} do not introduce new states deep in the band gap, but in preference shallow localized energy levels, such as the V_{Pb} acceptor level and La_{Pb} electron donor level. As the density of defects (or impurities) increases, the band structure of the crystal is perturbed by the potential of the defects as well as by the localized strains induced by the defects. At high density the discrete localized defect energy levels can turn into a continual energy band. The defect energy bands tend to overlap the conduction band and/or valence band of the crystal and the result is the optical gap contraction [22].

The concentration dependence of the absorption edge for PWO:La crystals can reasonably be ascribed to the combined effects of the above-mentioned polarization and localized defect energy level. Therefore, it can be understood quantitatively from the doping mechanism.

- (1) According to the Zhu's estimation [9], there are of order tens ppm V_{Pb} in the as-grown PWO. When the La³⁺ doping concentration is lower than double the intrinsic lead deficiency, (here, the sample containing 100 ppm La³⁺ is accepted), the incorporation of La³⁺ into the crystal is in the form of $[2La_{Pb}-V_{Pb}]$, which will lessen the intrinsic V_{Pb} concentration and simultaneously restrict the production of V_O in the crystal. The sum of defects in the material can be thought of as unchangeable. In other words, the main influence on the absorption edge comes from the polarization effect. Thus, the band gap widens and the highest value is observed in the crystal containing 100 ppm La³⁺.
- (2) In the case of PWO: xLa^{3+} ($x = 200$ and 400 ppm), the La_{Pb} concentration is more than that of $2[V_{Pb}]_{intrinsic}$ and all of the intrinsic V_{Pb} are depleted by the formation of $[2La_{Pb}-V_{Pb}]$. For the sake of the charge balance, many new V_{Pb} defects should be yielded. Consequently, the amount of defect in the material will grow. The effect of localized defect energy levels begins to exert an influence on the optical gap, but the predominant influence still arises from the polarization effect. As a result, the band gap values are between that of as-grown PWO and PWO doped by La³⁺ at 100 ppm.
- (3) On doping at higher concentration, for example, PWO crystals doped with La³⁺ at 1600 ppm, 2 and 8 mol%, more negative defects should be produced to keep the charge balance in the crystals, so the leading influence on the band gap is assigned to the effect of localized defect energy levels rather than polarization. Accordingly, evident red-shift of the absorption edge for these samples is found compared to that of as-grown PWO.

Will the V_{Pb} defect still play a unique role in the charge balance in the heavily La³⁺-doped PWO crystals? PWO can keep the scheelite structure well, even after heavily doping with La³⁺ by 15 mol% [23], but it cannot accommodate that much V_{Pb} in such a crystal [24]. It is inevitable that some other kind of negative centre should exist to neutralize the excess positive charges owing to heavy La³⁺ doping. Our FT-IR data (figure 5) help to further clarify the fact. The characteristic infrared absorption corresponding to W–O vibration appears in 1000–400 cm⁻¹; in particular the O–W–O stretches ($\nu_3A_u + \nu_3A_u$) occur in 900–750 cm⁻¹ [25].

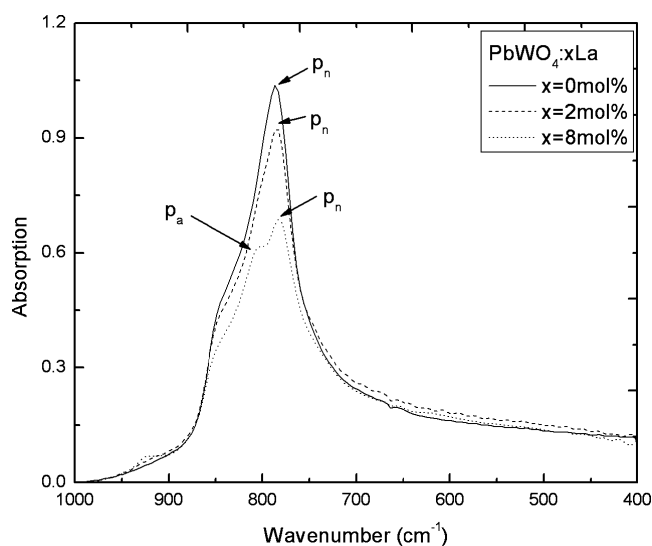


Figure 5. Infrared spectra of PWO:*x*La (*x* = 0, and 2, 8 mol%) crystals.

Figure 5 illustrates that a peak at $p_n = 785 \text{ cm}^{-1}$ exists in all samples and the spectrum of 2 mol% PWO:La crystal shows great similarities to that of the pure PWO. Obviously, the normal O–W–O stretches contribute to the peak at $p_n = 785 \text{ cm}^{-1}$. However, an additional peak centred at $p_a = 805 \text{ cm}^{-1}$ appears in the spectrum of the 8 mol% PWO:La crystal, which implies a new O–W–O stretch with a different chemical surrounding or different coordination from normal lattice oxygen. It could be O^- or interstitial oxygen ion (O_i^{2-}). Separate F^+ or O^- is claimed to be unstable in PWO crystals even at low temperature [21], and no evidence, for example, an ESR signal, is found for the existence of O^- in the entire temperature range. Therefore, it is reasonable to ascribe the new peak to the O–W– O_i stretches. The existence of O_i^{2-} in the lattice is supposed to be in the form of $[2(\text{La}_{\text{Pb}})-\text{O}_i]$ to maintain the charge balance competed with V_{Pb} and support the scheelite structure in heavily La^{3+} doped PWO crystals. The result is in accordance with our recent XPS and EXAFS measurements [9] and computer simulation result [26]. Acting as a localized defect energy level in the band gap, O_i has a similar influence on the absorption edge of the crystals as that of V_{Pb} .

4. Conclusion

Transmittance spectra of PWO:*x*La crystals were measured and a shift in the optical absorption edge is observed as a function of the added La^{3+} concentration. Both the energy gaps E_g and phonon energies E_p of crystals were calculated. The average phonon energy is estimated to be in the range of $242\text{--}274 \text{ cm}^{-1}$ for the pure and lightly La-doped PWO crystals. However, in heavily doped PWO crystals, the impurity assists the indirect transition instead of phonons. The variation of E_g can be interpreted by the combined effects of the polarization and localized defect energy level. The polarization effect may prevail in PWO crystals with low values of La^{3+} concentration (<400 at ppm), whose band gaps are broader than that of pure crystals. The localized defect energy level effect dominates in heavily La-doped PWO crystals (>1600 at ppm), in which a red-shift of the absorption edge was observed. Our FT-IR data of PWO:La crystals confirm that the existence of interstitial oxygen ion competes with V_{Pb} for charge balance in heavier doped PWO crystals.

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