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The optical and electrical properties in Nd^{3+} doped lead tungstate single crystals

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Abstract The influence of Nd^{3+} doping with different concentration on the luminescence properties of $PbWO_4$ single crystals were investigated by means of the thermo-luminescence, X-ray excited luminescence and photoluminescence spectra. Nd^{3+} doping has almost the same doping effects as that of La^{3+} doping in $PbWO_4$. The doping mechanism of Nd^{3+} was briefly discussed. Dielectric loss spectroscopy and conductibility were measured when the $PbWO_4$:Nd^{3+} single crystals were sequentially annealed in air atmosphere from 100 °C to 1000 °C. The heavily Nd^{3+}-doped $PbWO_4$ present a larger conductivity at the high temperature with low activation energy.

Introduction

Lead tungstate, $PbWO_4$ (PWO), is a new scintillating crystal that has large-scale application in high-energy physics due to its high density, short radiation length and fast decay time [1]. This crystal is a uniaxial crystal with the Scheelite structure [2], which is not closely packed and is so flexible that it has an ability to adjust itself to tolerate different kinds of defects (intrinsic and extrinsic defects).

Many different impurity ions have been doped in PWO to modify its scintillation characteristics. It has been demonstrated that doping with several tens of ppm of stable and large trivalent ions (A^{3+}), namely La^{3+}, Y^{3+}, Lu^{3+} and Gd^{3+}, in PWO could improve the transparency in the spectral region of scintillation emission (350–500 nm), radiation hardness [3–5]. An optimum doping concentration was found around 100 ppm in the case of Gd^{3+} doping [6]. The presence of trivalent ions efficiently compensates or diminishes various trapping centers, which is reflected in thermo-luminescence spectra [2]. Moreover, Kobayashi et al. has proposed a new heavy and radiation-hard Cherenkov radiators based on $PbWO_4$ doped with appropriate trivalent ions (such as La^{3+}, Gd^{3+}, Y^{3+}). Heavily doping with trivalent ions considerably reduces scintillation light intensity to a level lower than the Cherenkov light intensity, by keeping the excellent radiation hardness and causing no significant degradation in the short wavelength [7]. Further more, a beam test of this PWO Cherenkov radiator has been carried out [8].

Another factor is that $PbWO_4$ doped with rare earth (RE^{3+}) with rich $4f^9$ luminescence configuration, e.g. Er^{3+} or Nd^{3+}, could exist new luminescence properties. Nd^{3+} is one of the most intensively investigated ions. Kaminskii et al. have reported the pulsed and continuous wave laser actions in Nd^{3+}-doped $PbWO_4$ [9]. They carried out detailed investigations on the Raman spectra and Raman laser of $PbWO_4$ [10]. The total Stokes conversion efficiency beyond 50% has been achieved. Chen et al. had realized the self-stimulating Raman laser of Nd^{3+}-doped $PbWO_4$ with 56% optical frequency conversion efficiency [11]. The optical absorption,

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1064 nm emission and fluorescence lifetime, the intensity parameters and the absorption and emission cross section of Nd^{3+} ions in PWO host have been carefully investigated [12].

The aim of this paper is to report on influence of Nd^{3+} doping on the visible luminescence and electricity conductibility characteristics of $PbWO_4$ crystals. Luminescence properties were mainly investigated by thermoluminescence (TL), X-ray excited luminescence (XEL) and photoluminescence (PL) in a series of Nd^{3+} doped $PbWO_4$ crystals. The dielectric loss spectroscopy and conductibility were measured from 100 °C to 1000 °C.

Experimental

Nd^{3+} doped PWO crystals were grown with the doping concentrations of 150 ppm, 1.6, 2.0 and 2.5 at.% in the melt. The detailed grown procedure can be seen in Ref. [12]. The crystal samples used for spectral experiments were cut to a rectangle with dimensions of $15 \times 15 \times 2$ mm^3 and were perpendicular to the *c*-axis. All the surfaces of the rectangle were finely polished.

XEL spectra were measured by a FluorMain, X-ray excited Spectrometer and operated under the same condition (80 kV, 4 mA) at room temperature (RT). The luminescence spectra were obtained by 44 W plate grating monochromator and Hamamatsu R928-28 photomutiplier. Photoluminescence spectra were taken using a fluorescence spectrophotometer (Perkin Elmer LS-55) with a Xenon lamp as an excitation source. Thermo-luminescence samples with dimensions of $8 \times 8 \times 1$ mm^3 were first thermally treated for 100 min at 200 °C in darkness to remove any excess color centers; The TL investigations after UV light irradiation were performed on FJ-427A thermo-luminescence spectrometer with a heating rate of 2 K/s. A 500 W high-pressure mercury lamp was used for irradiating the samples for 15 min.

For the recording of dielectric spectra, platinum layers were sputtered on two surfaces of the samples as the electrodes; The electrical measurements were applied on a *HP* Agilent 4294A Precision Impedance Analyzer that scanned between 40 Hz and 110 MHz, and could hold the sample at a constant temperature from ambient temperature to 1300 °C. The samples were put in the closed cylinder furnace and connected to a PC thermometer controller via 16048A Cables. The experiments were designed as the following procedure: The samples were sequentially heated over the temperature range of 100–1000 °C at a 100 °C temperature interval. Each frequency sweep measurement was conducted after the set temperature point had been stabilized for 40 min to ensure thermal uniformity in the sample.

Results and discussions

The TL glow curves between room temperature (RT) and 623 K for pure PWO and PWO:Nd^{3+} 150 ppm after UV irradiation are shown in Fig. 1. There exist at least two TL peaks centered at 324 and 404 K in the pure PWO. The TL curves of PWO:Nd^{3+} 150 ppm show nearly the straight line, no TL peaks appeared; and the other Nd^{3+} samples have the same profile, even in the case of heavily doped (2.5 at.%) sample. This is a significant lowering sign of intrinsic lattice defects. Although Nd^{3+} is an active luminescence ions with the rich irradiative configuration, its suppression of intrinsic lattice defects in PWO has the same effects with the other inertial luminescence trivalent RE^{3+} ions, such as La^{3+}, Y^{3+} and Gd^{3+} ions [13, 14].

XEL spectra of samples are presented in Fig. 2. Increasing Nd^{3+} doping concentration from 150 at. ppm to 1.6 and 2.5 mol%, the luminescence of PWO:Nd^{3+} became weaker and weaker and were dominated by blue luminescence component. XEL spectra of PWO:Nd^{3+} has similar luminescence component to that of radioluminescence of PWO:La^{3+} crystal [15]. The PWO:Nd^{3+} 2.5 mol% decreased its luminescence intensity by a factor of 8 compared to that of undoped PWO, which was so weak that luminescence spectra presented nearly a straight line. Several broad luminescence bands between 450 and 650 nm on PWO:Nd^{3+} might created by the absorption of Nd^{3+} ions.

The PL spectra are shown in Fig. 3(a, b), which has a similar variety to results of XEL in Fig. 1. According to emission spectra measured under the same conditions, the total luminescence of PWO is gradually suppressed on the samples by Nd^{3+} doping levels from 150 ppm to 1.6 at. and 2.5 at.%. The luminescence and scintillation spectra of

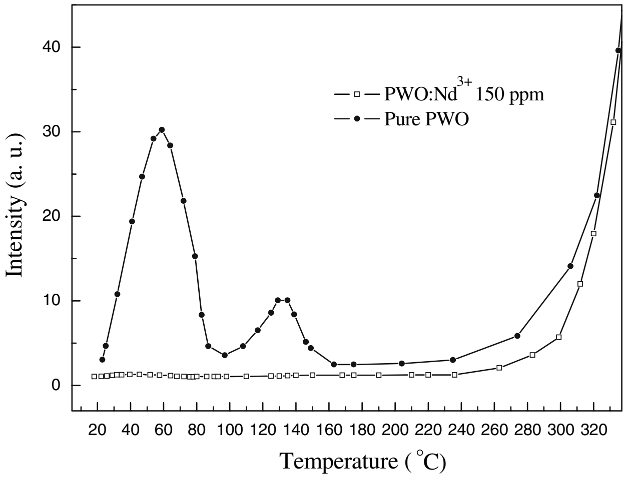

Fig. 1 TL spectra of pure PWO and PWO:Nd^{3+} 150 ppm crystals under UV radiation for 15 min

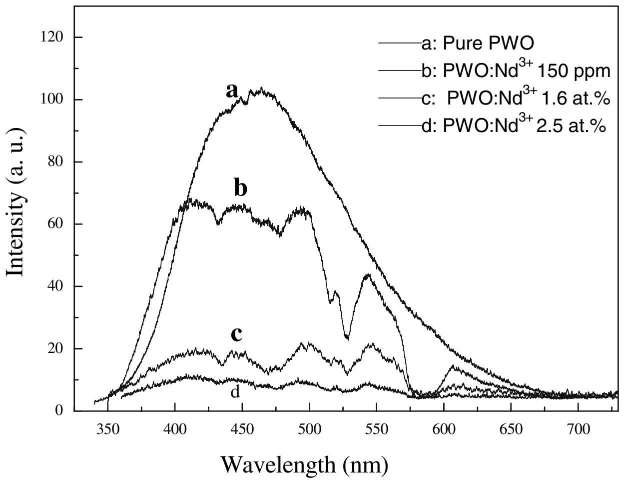

Fig. 2 The X-ray excited luminescence spectra of undoped PWO crystal and Nd^{3+} doped PWO samples at RT. (**a**): Pure PWO, (**b**): PWO doped with 150 at. ppm Nd^{3+}; (**c**): 1.6 mol% and (**d**): 2.5 mol% of Nd^{3+}

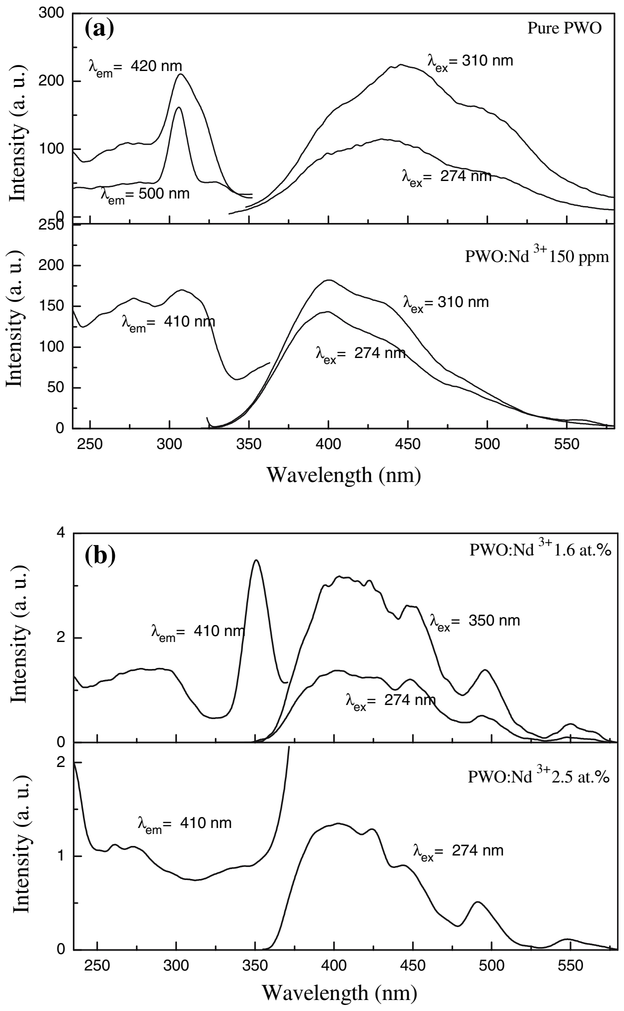

Fig. 3 The excitation and emission spectra (a): pure PWO and PWO:Nd^{3+} 150 ppm, (**b**):PWO:Nd^{3+} 1.6 at % and 2.5 at%

PWO show the so-called blue (420 nm) and green (480–520 nm) components. The former component is an exciton emission ascribed to a $(WO_4)^{2-}$ molecular anion, while the latter belongs to the WO_3 group or can be also induced by the Mo^{6+} ion $(MoO_4)^{2-}$ group (for review, see [2]). In the emission spectra of pure PWO, a stronger emission at 450 and 500 bands and weaker one at around 400 nm bands were observed. With the Nd^{3+} doping, the emission bands from 480- to 600-nm were greatly suppressed, while 400 nm emission is dominated on the emission spectra of PWO: Nd^{3+}. That is to say, just like La^{3+} doped sample [16], the emission in Nd^{3+}-doped PWO get a depressed green emission and is dominated by the blue luminescence components compared with that of pure PWO.

On excitation spectra of 410 emission (an exciton emission), excitation peak at 310 nm (an exciton excitation) shifts to short wavelength, becomes weaker and weaker and almost disappears on that of PWO doped with Nd^{3+} 1.6 mol% and 2.5 mol%. It indicates the heavily doping Nd^{3+} ions annihilate intrinsic lattice defects, resulting in intensively suppressing exciton luminescence efficiency of PWO.

In PWO:Nd^{3+} crystal, EPR (electron paramagnetic resonance) results have confirmed that Nd^{3+} ion replaces the Pb^{2+} ion [17]. Because of the similar chemical properties between Nd^{3+} La^{3+} ions, and nearly the same doping effects at different doping concentration mentioned above, i.e., influence of Nd^{3+} doping on the TL and PL spectra, it is reasonable to suggested that in Nd^{3+} doped PWO the doping mechanism should be the same as that of PWO:-La^{3+}. That is to say, the positive charge caused by substitution of Nd^{3+} ions on the Pb^{2+} lattice could be balanced by V_{Pb}, $[2\left(Nd_{Pb}^{3+}\right)^{\cdot}-V_{Pb}'']$ [18].

In heavily Nd^{3+}-doped PWO, the electrical properties, especially the high temperature conductivity, were investigated. The impedance spectra were measured at different annealing temperature from 100 °C to 1000 °C, which has been widely used to characterize dielectric behavior of single crystal and polycrystalline and to provide a physical representation of the relaxation mechanism. Figure 4 present the dielectric loss factor (tan δ) as a function of frequency for PWO:Nd^{3+} 1.6 at.%. The other samples are similar (figures are omitted for brevity). The loss factor maximum shifts to higher frequencies as the temperature rise. When the samples were measured at a temperature above 800 °C, the loss peak disappeared gradually, and dielectric behavior present nearly a straight line, perhaps because of the larger conductivity at high temperature.

As described detailed in the reference [18] of La^{3+}, Y^{3+} and Gd^{3+} doped PWO, this relaxation peak could be ascribed to the dipole complexes $[2\left(Nd_{Pb}^{3+}\right)^{\cdot}-(V_{Pb})'']$ formed by the Nd^{3+} substitution of Pb^{2+} site, combining with the intrinsic Pb^{2+} vacancy. The relaxation can be fitted by

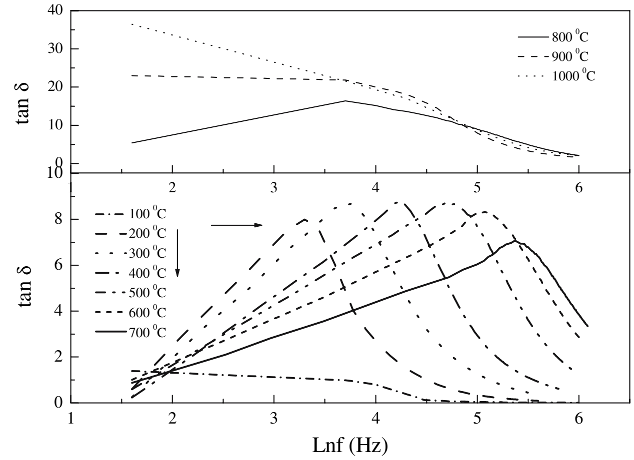

Fig. 4 The dielectric loss relaxation spectra of PWO:Nd^{3+} 1.6 at.% crystal at different temperatures

Arrhenius equation with a single relaxation time τ, which varies with temperature T in an exponential manner,

$$f_{\max} = \frac{1}{\tau} = \nu_0 \exp\left(\frac{-E}{kT}\right) \quad (1)$$

where E is the activation energy for the relaxation process, ν_0 is the frequency factor and k is the Boltzmann constant. The frequency $f_{\max}$ at which the maximum loss occurs is shown in Fig. 5. In this way, the activation energy E is determined to be 0.53 ± 0.02 eV, which is lower than that of heavily doped PWO:La^{3+} (0.78 eV) [19].

In a search for new high temperature ionic conductors, various substituted Scheelite-type samples were prepared and their electrical conduction was investigated. Typical Scheelite-type oxides can be regarded as double oxides with a deformed fluorite-type structure. As lead and tungsten have almost the same electronegativity, the PWO Scheelite-type structure could be seen as a double oxide of the deformed fluorite-type, where lead and tungsten atoms are assumed to be equivalent in the crystal. Thus PWO is suitable as an oxide ion conductor [20]**.** In K^{+}, Bi^{2+}, Y^{3+} and La^{3+} doped PWO, the conductivity experiments have confirmed that V_{O} were the main charge carriers [21]. So it is necessary to check their conductivity, especially at higher temperature in the PWO:Nd^{3+} with induced V_{O}. The conductivity in PWO:Nd^{3+} 1.6 at. % and 2.5 at.% crystals at the elevated temperatures from 1 to 1 MHz showed that the Nd^{3+} doping considerably enhanced the conductivity with an increase in the temperature above 700 °C. Such conductivity behaviors indicate that PWO become to exhibit higher conduction at high temperature by Nd^{3+} doping. In the pure PWO, the conductivity was indicated to be fairly low (5.0×10^{-5} S cm^{-1} at 800 °C) [22]. Conductivities of PWO:Nd^{3+} 1.6 at.% crystal were measured to be 9.81×10^{-3} S cm^{-1} and 7.16×10^{-3} S cm^{-1} at 1000 °C and 800 °C, respectively. The Arrhenius plots of conductivity are presented in Fig. 6. The activation energy in the PWO:Nd^{3+} 1.6 at.% and PWO:Nd^{3+} 2.5 at.% were evaluated to be 0.33 ± 0.01 eV and 034 ± 0.01 eV, respectively. Taking into account of its larger conductivity at the high temperature with this relatively low activation energy, this Nd^{3+} doped scintillating crystal would be expected to posses a potential application as fast ion conductors.

Conclusions

TL peaks existed in the pure PWO disappeared for all PWO:Nd^{3+} samples. The results of XEL and PL spectra show that luminescence of PWO are greatly suppressed due to the Nd^{3+} ions doping. The emission in Nd^{3+}-doped PWO get a depressed green emission and is dominated by the blue luminescence components. The intrinsic 310 nm

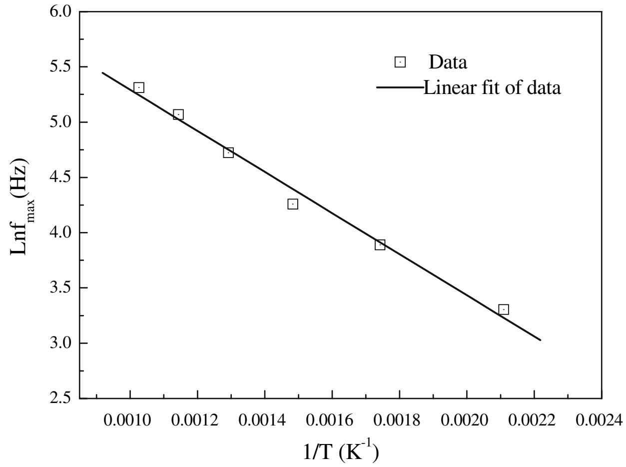

Fig. 5 Lnf$_{\max}$–1/T plot of PWO:Nd^{3+} 1.6 at.% crystal

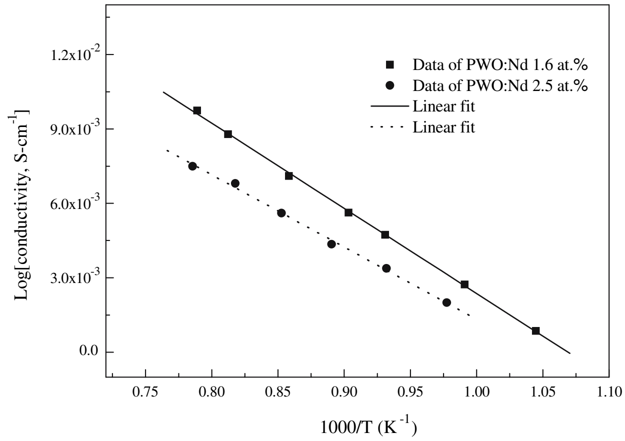

Fig. 6 Arrhenius plot of conductivity of PWO:Nd^{3+} 1.6 at. % crystal

exciton excitation gradually disappeared with increasing Nd^{3+} doping concentration from 150 ppm to 2.5 at.%. Although Nd^{3+} is an active luminescence ion with the rich irradiative configuration, it has the same influence on the luminescence of $PbWO_4$ as the other inertial luminescence trivalent RE^{3+} ions, such as La^{3+}, Y^{3+} and Gd^{3+}. The Nd^{3+} heavily doped samples have a larger conductivity at the high temperature with low activation energy. This would be useful for the purpose of application as the fast ion conductors.

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