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Observation of dipole complexes in $PbWO_4$:La^{3+} single crystals

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The frequency dependence of dielectric loss factor (tan δ) in undoped and La-doped $PbWO_4$ crystals has been investigated over a frequency range from 10 Hz to 10 MHz and a temperature range from 40 to 370 °C. A typical dielectric relaxation phenomenon in $PbWO_4$:La^{3+} has been observed. Experimental results indicate that there exist intrinsic mobile defects in pure $PbWO_4$ crystals and lead vacancies are the predominant mobile defects. In La-doped $PbWO_4$ crystals, La^{3+} ions may be located at the Pb^{2+} sites and combine with lead vacancies to form the dipole complexes $[2(La_{Pb}^{3+})^{\bullet}-V_{Pb}'']$, which may be the origin of the dielectric relaxation phenomenon in $PbWO_4$:La^{3+} crystals. © *1998 American Institute of Physics.* [S0021-8979(98)08317-0]

I. INTRODUCTION

The scintillating properties of $PbWO_4$ (PWO) have been investigated intensively in recent years since they have been selected as the scintillating material in the CMS of a large hadron collider (LHC),[1–3] at CERN, Geneva. The high energy applications involve such a severe radiation environment that the research of radiation damage mechanisms and the improvement of radiation hardness of PWO crystals become rather important. Recently, La^{3+} doping of PWO crystals has attracted much attention, for it can effectively improve the transmission and radiation hardness of PWO crystals.[4] Moreover, La doping seems to be an efficient tool in removing trap centers active in both TSL and recombination decay processes below room temperature (RT) and at RT, respectively.[5] Among numerous articles about the scintillating properties of PWO crystals, it was found that the interpretations of the radiation damage mechanisms and La doping effects are mainly based on several basic assumptions: (i) PWO crystals tend to be ‘‘lead deficient’’ because of the evaporation of PbO during crystal growing process. (ii) Lead vacancies as negative charge centers induce the appearance of positive charge centers, i.e., Pb^{3+}, O^- hole centers which are the origin of 350 and 420 nm absorption bands[6] that in turn result in the degradation of the transmission and radiation hardness of PWO crystals. (iii) La^{3+} ions at Pb^{2+} sites introduce an excess charge into the Pb sublattice, thus reducing the density of Pb^{3+}, O^- hole centers. Therefore the transmission and radiation hardness of PWO crystals are improved.

However, so far there has been no direct evidence from microstructural studies to support the existence of lead vacancies and the La^{3+} charge compensation mechanism. In the present work, a typical dielectric relaxation phenomenon in PWO:La^{3+} crystals has been observed, and experiments provide convincing proof of the existence of Pb vacancies and a La^{3+} charge compensation mechanism.

II. EXPERIMENTS

Three PWO crystal ingots were grown from 5 N purity raw powders by the improved Bridgman method, to obtain undoped and La-doped PWO crystals ($L1$ and $L2$ with 150 and 500 ppm of La in the melt, respectively). Three samples for ac impedance analysis were cut from the ingots near the crystal seed. Dimensions of the samples were about $10\times10\times1$ mm, with their 10×10 mm^2 faces perpendicular to the c axis of the crystals, and coated with an Ag electrode. An impedance analyzer (Hewlett Packard, HP4192A) was used for measuring the real and imaginary parts of the dielectric constants. Its measurement limitation is $10^{-9}\ \Omega^{-1}$. Measurements were carried out over the frequency range of 10 Hz–10 MHz with 72 samplings, in steps of 5 °C in the temperature range of 40–370 °C. Electron spin resonance (ESR) measurements at 300 K were carried out in a Brüker ESR spectrometer operating in the X-band frequency.

III. RESULTS AND DISCUSSION

Figure 1 presents the frequency dependence of dielectric loss factor (tan δ) in undoped (a) and La doped (b) PWO crystals at 250 °C. The undoped PWO crystal shows almost no response to the variation of frequency, while a typical dielectric relaxation phenomenon has been observed in La-doped crystal. Its dielectric loss curve displayed a symmetric distribution. The experimental results at temperatures above 150 °C are similar to the results at 250 °C. On the basis of the fact that the maximum dielectric loss frequency is in the range of kHz–MHz and the activation energy of the relaxation process (the detailed calculation process is presented in a later section) is in the range of 0.49–0.55 eV, the origin of dielectric relaxation behavior in PWO:La^{3+} may be ascribed to the dipole association of defects.[7]

A useful means of analyzing the dielectric relaxation behavior is the Cole–Cole plot showing the relation between the real part (ϵ') and imaginary part (ϵ'') of the dielectric constant. The Cole–Cole plots of $L2$ (500 ppm La doping) at 150 °C (a) and 353 °C (b) are shown in Fig. 2. The small deviation of the plot at 150 °C from perfect semicircle indi-

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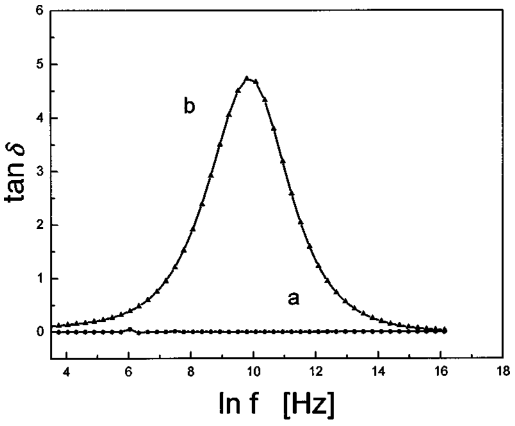

FIG. 1. The frequency dependence of dielectric loss factor (tan δ) in undoped (a) and La-doped (b) $PbWO_4$ crystals.

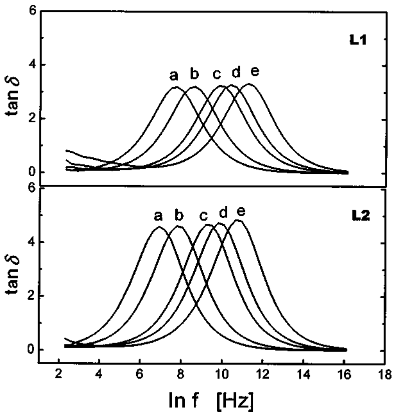

FIG. 3. The dielectric loss relaxation spectra of $PbWO_4:La^{3+}$ crystals $L1(150\,\mathrm{ppm}\,La^{3+})$ and $L2(500\,\mathrm{ppm}\,La^{3+})$ at different temperatures: (a) 172 °C, (b) 199 °C, (c) 252 °C, (d) 279 °C, (e) 337 °C.

cates that the dielectric relaxation behavior of La-doped PWO crystals is a single relaxation process and can be described by the Debye equation approximately. Additionally, a branch extends from the semicircle in the plot at 353 °C. The above variation is commonly originated from mobile defects, which become active at high temperature and result in dc conductivity.[7] The results shown above indicate that in addition to the dipole association of defects, there also exist mobile defects in $PbWO_4:La^{3+}$ crystals.

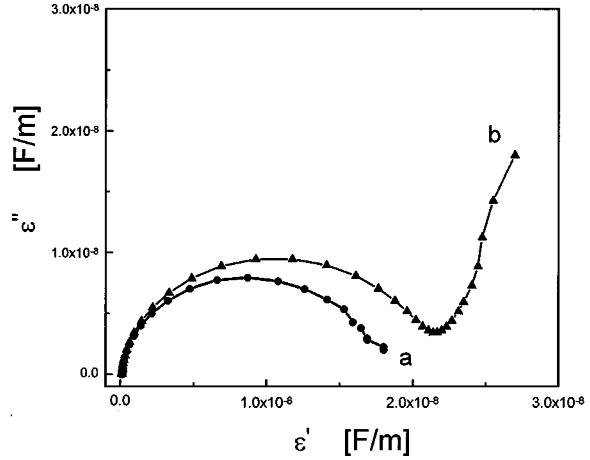

FIG. 2. The Cole–Cole plots of $L2$ (500 ppm La^{3+}) at 150 °C (a) and 353 °C (b).

Figure 3 illustrates the dielectric loss relaxation spectra of $L1$ and $L2$ at different temperatures. The tan δ maximum shifts to the higher frequencies as the temperature increases. Meanwhile, the dielectric loss caused mainly by dc conductivity[7] increases gradually. Moreover, there are some differences between $L1$ and $L2$. (i) In high frequency range, the dielectric loss of $L2$ caused by the dipole association of defects is higher than that of $L1$. (ii) In low frequency range, the dielectric loss of $L1$ caused by the mobile defects is higher than that of $L2$. (iii) At the same temperature, the maximum dielectric loss frequency of $L1$ is higher than that of $L2$. When single dielectric relaxation process and dc conductivity exist simultaneously, the dielectric loss factor is given by

$$\tan\,\delta=\frac{\gamma+\epsilon_0(\epsilon_s-\epsilon_\infty)\,\dfrac{\omega^2\tau}{1+(\omega\tau)^2}}{\omega\epsilon_0\epsilon_s}, \tag{1}$$

where ϵ_0 is the dielectric permittivity of free space, ϵ_s is the static dielectric constant, ϵ_∞ is optic frequency dielectric constant, ω is the angular frequency of applied electric field, τ is relaxation time, and γ is the dc conductivity rate. In low frequencies $(\omega\tau\ll 1)$, the relation reduces to

$$\tan\,\delta=\frac{\gamma}{\omega\epsilon_0\epsilon_s}. \tag{2}$$

Assuming that the kind of mobile defects in the three samples are identical, at the same temperature and frequency $(\omega\tau\ll 1)$, tan δ varies only with the concentration of mobile defects. In experiments, the imaginary and real parts of the ac conductivity in low frequencies (especially below 50 Hz) were so small that they approached the measurement limit $(10^{-9}\,\Omega^{-1})$. Although it was difficult to measure more accurate dielectric loss values at low frequencies (below 50 Hz), the experimental results have already provided us with significant information. At $T=250\,°\mathrm{C}$ and $f=10\,\mathrm{Hz}$, the tan δ in undoped samples: $L1$ (150 ppm) and $L2$ (500 ppm) is 0.8, 0.4, and 0.1, respectively. These data give us important information about the microstructure in PWO crystals: (1) The mobile defects, causing low frequency dielectric loss, are intrinsic defects of pure PWO crystals. (2) The concentration of mobile defects decreased as the La doping concentration increased.

On the other hand, the concentration of dipoles in La-doped PWO crystals, based on the Debye equation, is determined by the maximum of the imaginary part of the dielectric constant. At $T=250\,°\mathrm{C}$, the concentration of dipoles in $L2$ is 1.84 times that in $L1$. The results shown above illustrate clearly that when La doping concentration rose, the concentration of mobile defects in PWO crystals decreased, whereas that of dipole complexes increased.

The activation energy for the dipole complexes in $L1$ and $L2$ can be determined from the frequency and the tem-

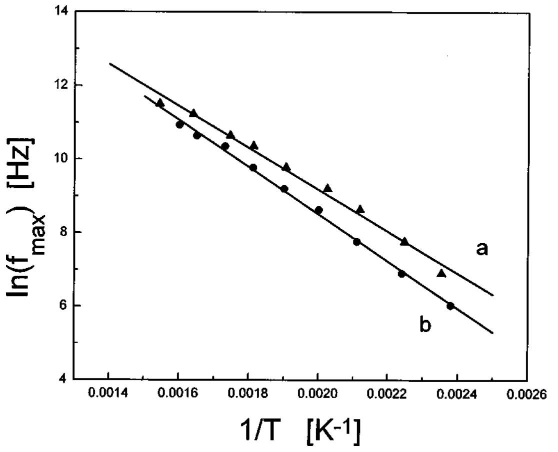

FIG. 4. The $\ln(f_{\max})-1/T$ plots of $L1(150\,\mathrm{ppm\,La}^{3+})$ (a) and $L2(500\,\mathrm{ppm\,La}^{3+})$ (b).

perature dependence of the relaxation peaks. The frequency $f_{\max}$ at which the maximum loss occurs is shown in Fig. 4 as a function of temperature. The plots of In $f_{\max}$ vs $1/T$ are linear, indicating a relationship of the form $f_{\max}=1/\tau=\nu\exp(-E/kT)$, where τ is the relaxation time, E the activation energy for the relaxation process, ν a frequency factor, and k the Boltzman constant. In this way we determine for $L1(150\text{ ppm})$ and $L2(500\text{ ppm})$ that E is 0.49 ± 0.02 and 0.55 ± 0.01 eV, respectively, and their ν is on the order of 10^{-11} s.

To understand the nature of the dielectric relaxation phenomenon in PWO:La^{3+} crystals, we must consider a group of associated defects which give rise to a dipole. PWO crystals possessing sheelite structure are comprised of two substructure units Pb^{2+} and WO_4^{2-}. When La^{3+} ions are introduced, because they are similar in electric charge and ionic radius (La^{3+}:1.15 Å, Pb^{2+}:1.20 Å) to Pb^{2+} ions, it is reasonable to assume that they occupy the Pb^{2+} sites. The dielectric relaxation phenomenon in KCl:Mg^{2+} crystals has been investigated intensively,[8] Mg^{2+} occupies the K^{+} sites and induce the emergence of K^{+} vacancies to recover charge balance. The associations of the defects $[(\mathrm{Mg}_K^{2+})^{\bullet}-V_K']$ are the origin of the dielectric relaxation phenomenon in KCl:Mg^{2+} crystals. The relaxation behavior in PWO:La^{3+} is similar to that in KCl:Mg^{2+}. Both of them are determined by single relaxation time and their activation energies for dipole are close to each other (PWO:La^{3+}:0.49–0.55 eV, KCl: Mg^{2+}:0.46–0.52 eV). It is therefore reasonable to consider $[2(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-V_{\mathrm{Pb}}'']$ to be the most plausible basic structure of the dipole complexes in La-doped PWO crystals.

However, there may also exist another kind of dipole structure, i.e., $[(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-(\mathrm{W}_{\mathrm{W}}^{5+})']$ formed by W^{6+} transforming to W^{5+}. It is known that W^{5+} are paramagnetic ions and the measurement limitation of the ESR method is higher than that of the dielectric relaxation method. If $[(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-(\mathrm{W}_{\mathrm{W}}^{5+})']$ were the dominant parts of dipole complexes in PWO:La^{3+} crystal, the ESR signal of W^{5+} should be observable. The ESR spectra of $L2$ was then measured carefully. No significant signal which could be ascribed to the W^{5+} was observed. So the possibility of the existence of this kind of dipole association has been excluded. Moreover, although there exist some kinds of color centers in PWO crystals, the dielectric loss in PWO:La^{3+} may not be ascribed to the color centers dipole relaxation, i.e., electron jumping between various positions around color centers, because the activation energy and frequency factor of this kind of relaxation process are on the order of meV and 10^{-6} s, respectively, far in magnitude from the data obtained in the experiments.[9–11] Therefore, we conclude that the nature of the dielectric relaxation phenomenon in PWO:La^{3+} is related to the dipole complexes $[2(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-V_{\mathrm{Pb}}'']$, furthermore, the predominant parts of mobile defects in PWO crystals are probably lead vacancies, based on the fact that the mobile defects decreased as La doping increased.

At $T=250\,°\mathrm{C}$, $f=10$ Hz, the $\tan\delta$ of undoped samples, $L1$ and $L2$ is 0.8, 0.4, and 0.1, respectively. According to Eq. (2), their concentration of mobile lead vacancies may be represented as $0.8a$, $0.4a$ and $0.1a$, respectively. The degradation of mobile lead vacancies in La-doped crystals results from the combination of La^{3+} ions with lead vacancies. So the concentration of dipole associations $[2(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-V_{\mathrm{Pb}}'']$ in $L1$ and $L2$ is $(0.8a-0.4a)$, $(0.8a-0.1a)$, respectively. The dipole concentration of $L2$ is about twice that of $L1$. This preliminary theoretical estimation is in good agreement with the experimental result of 1.84. It is difficult to make a more accurate estimation, for the experimental accuracy of ac conductivity in low frequencies is limited by equipment and the actual defect structure of PWO crystals is very complex. Yet, this estimation further supports our conclusion that lead vacancies are the intrinsic defects of pure PWO crystals and the basic structure of dipole complexes in La-doped crystals is $[2(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-V_{\mathrm{Pb}}'']$.

Finally, we offer an interpretation of the fact that the sample with a lower La doping concentration has lower dipole activation energy $[L1(150\,\mathrm{ppm})$: 0.49 eV, $L2(500\,\mathrm{ppm})$: 0.55 eV$]$. The nature of the impurity–vacancy $(I-V)$ dipole dielectric relaxation process is related to vacancies jumping between different equilibrium positions separated by a potential barrier. In La-doped PWO crystals, there exist unassociated (free, mobile) lead vacancies near to the dipole complexes $[2(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-V_{\mathrm{Pb}}'']$, which affected the relaxation process in two aspects: (i) providing more probability for the jumping of associated lead vacancies during relaxation process, and (ii) loosening the local crystal environment of the dipole complexes, thus decreasing the potential barrier that separated the equilibrium positions of dipole. In short, the existence of unassociated V_{Pb} enhances the reorientation of the dipole complexes $[2(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-V_{\mathrm{Pb}}'']$. $L1$ (150 ppm) possesses a higher concentration of unassociated lead vacancies than $L2$ (500 ppm), thus showing lower dipole activation energy on the whole. This is a preliminary interpretation of the experimental results and detailed work is still ongoing.

IV. CONCLUSION

Our experiments show that PbWO_4:La^{3+} possesses characteristic dielectric relaxation behavior, which may be originated from the dipole complexes with the basic form $[2(\mathrm{La}_{\mathrm{Pb}}^{3+})^{\bullet}-V_{\mathrm{Pb}}'']$. In pure PbWO_4 crystals, there exist mobile defects, of which the predominant parts are probably lead vacancies. The doping La^{3+} may be located at the Pb^{2+} sublattice sites, and combine with lead vacancies to form the dipole complexes $[2(La_{Pb}^{3+})^{\bullet} - V_{Pb}'']$. This shows clearly that for the nonstoichiometric crystals like $PbWO_4$ grown from the melt, the lead vacancies may exist as a kind of intrinsic defect, and will play an important role in the formation of color centers under ionic radiation.

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