VIBRATION AND LUMINESCENCE SPECTROSCOPIC INVESTIGATIONS OF THE ALKALI RARE EARTH DOUBLE PHOSPHATES $M_3(RE, Eu)(PO_4)_2$ (M = K, Rb; RE = La, Gd)*

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Dedicated to Prof. Dr. Detlef Haberland on his 60th birthday

The room temperature IR- and Raman spectra of the different $M_3RE(PO_4)_2$ (M = K, Rb; RE = La, Eu, Gd) double phosphates were analysed and used to interpret the vibronic side band structure in the photoluminescence spectra. The intraconfigurational $4f-4f$ electronic transitions in the photoluminescence spectra of the Eu^{3+} doped $M_3RE(PO_4)_2$ were analysed in detail. The crystal field fine structure of the $^5D_0 \rightarrow ^7F_J$ (J = 0−4) transitions was analysed accounting for the information on the crystal structure. The effect of the temperature as well as the alkali host cation was evaluated. Finally, a preliminary crystal field energy level scheme for the ^7F_J (J = 0−4) ground term was deduced from the analysis of the photoluminescence as well as IR- and Raman spectra.

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1. Introduction

Alkali rare earth double phosphates of the type $M_3RE(PO_4)_2$ (M = K, Na) have been studied by several authors [1–5], but not much is known about the spectroscopic properties of the analogous rubidium compounds. Preparation and lattice parameters of some rubidium rare earth double phosphates have been described by Melnikov et al. [6, 7]: $Rb_3(RE, Eu)(PO_4)_2$ (where RE is lighter

than Dy) crystallize in the monoclinic system with the space group $P2_1/m$ (No. 11 in [8], $Z = 2$) as do the potassium compounds [4]. The potassium and rubidium lanthanum double phosphates form crystalline solid solutions without any miscibility gap [9].

The broad band gap of approximately 8 eV typical to isolator compounds [7] provides a suitable environment for a detailed study of the luminescence processes involved in the electronic transitions of the RE^{3+} ions within the $4f$ electron shell. The trivalent europium ion in the rare earth lattice sites was used to probe the environment of the emission center in these hosts: in contrast to the sodium compounds [2], there is only one rare earth lattice site in the potassium and rubidium ones [3]. In continuation to the former investigations, the spectroscopic properties of the $M_3(RE, Eu)(PO_4)_2$ (M = K, Rb; RE = La, Eu, Gd) system are now reported concentrating especially on the europium doped rubidium lanthanum and gadolinium double phosphates.

2. Experimental

2.1. Sample preparation

The $K_3RE(PO_4)_2$ and $Rb_3RE(PO_4)_2$ (RE = La, Eu, Gd) powder samples were prepared by a solid state reaction between the stoichiometric amounts of RE-phosphate hydrate, potassium and rubidium carbonates and dihydrogen phosphates, which were ground and then heated in air at temperatures between 1000 and 1200 K [6, 9, 10]. $REPO_4 \cdot nH_2O$ and the alkali phosphates were prepared by precipitation from the corresponding solutions by phosphoric acid. The homogeneous solution of the RE^{3+} ions was obtained by dissolving the high purity oxides (99.999%) in nitric acid [9].

Thermoanalytic measurements (Setaram TG-DTA 92) were used to optimize the conditions of the solid state reaction. The X-ray powder diffraction analyses with a HZG4 Goniometer (Feinmechanik Freiberg) confirmed the purity and structure of the synthesized phases. FT-IR investigations were carried out on a Perkin Elmer Spectrometer 2000 FT-IR apparatus while for the FT-Raman spectroscopic studies, a Bruker FRA 106 Spectrometer with YAG:Nd laser radiation at 1064 nm was used. For luminescence measurements the $M_3RE(PO_4)_2$ phases were doped with 5 mole-% of Eu^{3+}.

2.2. Luminescence measurements

The luminescence spectra of the whitish $M_3(RE, Eu)(PO_4)_2$ (M = K, Rb; RE = La, Gd) powders were measured with UV excitation from a low pressure mercury discharge lamp by using a metal interference filter to select the 254 nm line. Additional mercury lines above 300 nm were removed with a wide band filter placed in front of the sample. An edge filter (< 450 nm) behind the sample eliminated the reflected excitation radiation. The luminescence measurements were carried out both at the room and liquid nitrogen temperatures. The luminescence spectra of the samples were measured by an optical set-up consisting of a single photon counting Hamamatsu R1463-01 photomultiplier, a 0.5 m Czerny–Turner

type ARC monochromator (resolution: 0.05 nm) and a liquid N_2/He cryostat equipped with an optical head (Oxford Instruments). The $^5D_1 \rightarrow {}^7F_J$ and $^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) transitions were recorded in the range from 520 to 715 nm.

3. Results and discussion

The IR absorption spectra of the double phosphates (Fig. 1) are quite similar irrespectively of the potassium or rubidium, as well as of the lanthanum, europium, or gadolinium host cations. Only PO_4 vibrational modes could be found with certainty: in the region from 450 to 650 cm^{-1} the deformation and between 900 and 1300 cm^{-1} the stretching modes [11]. The absence of the P–O–P modes indicates that no bridging oxygen atoms (e.g. the diphosphate groups) are present [12]. The compounds can thus be characterized as island phosphates. The weak bands below 450 cm^{-1} probably correspond to the RE–O vibrations [13]. Nine vibrational modes are to be expected for the five atoms in PO_4 according to $3N - 6 = 9$. Due to the low point symmetry of the RE^{3+} site no degenerate vibrational modes exist. According to the crystallographic data, there exist two different non-equivalent PO_4 tetrahedra and thus more than the maximum number of the theoretically expected modes for one PO_4 tetrahedra was observed [4].
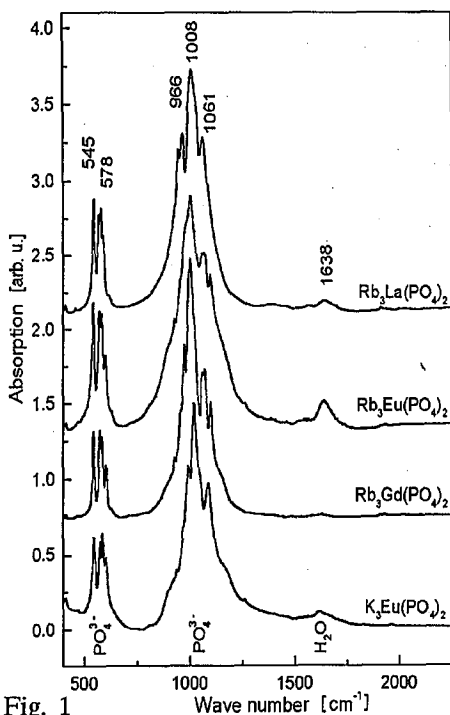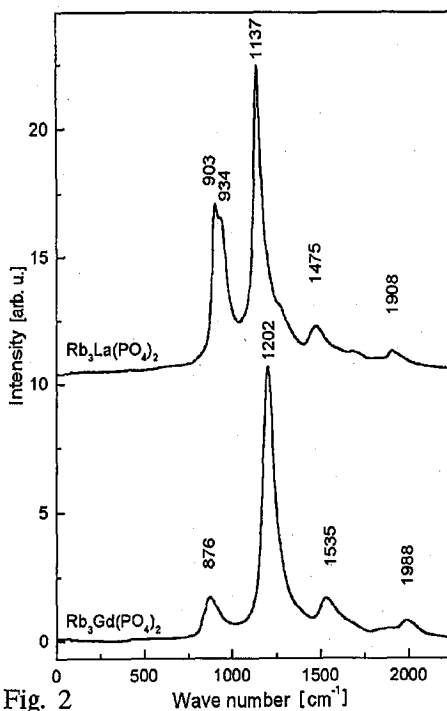

Fig. 1.

Fig. 2.

Fig. 1. FT-IR absorption spectra of $Rb_3RE(PO_4)_2$ and $K_3Eu(PO_4)_2$ (RE = La, Eu, Gd).

Fig. 2. FT-Raman spectra of $Rb_3RE(PO_4)_2$ (RE = La, Gd).

The Raman spectra (Fig. 2) of $Rb_3La(PO_4)_2$ as well as $Rb_3Gd(PO_4)_2$ show broad bands of low resolution near the stretching modes of the PO_4 tetrahedra (La: 920 and 1137 cm^{-1}; Gd: 876 and 1202 cm^{-1}). The additional lines out of this range, above 1600 and at 2000 cm^{-1} might be due to absorbed water on the sample surface and overtone vibrations, respectively. The larger splitting of the Raman lines for the rubidium gadolinium double phosphate (326 cm^{-1}) in comparison to the lanthanum compound (217 cm^{-1}) may be due to the more distorted PO_4 tetrahedra in the gadolinium phosphate as supported by the crystallographic information derived from the Rietveld analyses of the X-ray diffraction pattern of these compounds [14].

A comparison between the IR and Raman spectra of the gadolinium or europium doped gadolinium compounds (Fig. 3) show very weak lines in the Raman spectra corresponding approximately to the infrared active vibrations. The vibrational selection rules are thus not strictly valid.

The luminescence spectra of the potassium and rubidium europium double phosphates show the characteristic yellow-red emission of the trivalent europium ion (Fig. 4) owing to the intraconfigurational electronic $^5D_0 \rightarrow {}^7F_{0-4}$ transitions. The lone sharp $^5D_0 \rightarrow {}^7F_0$ transition indicates that only one kind of luminescence
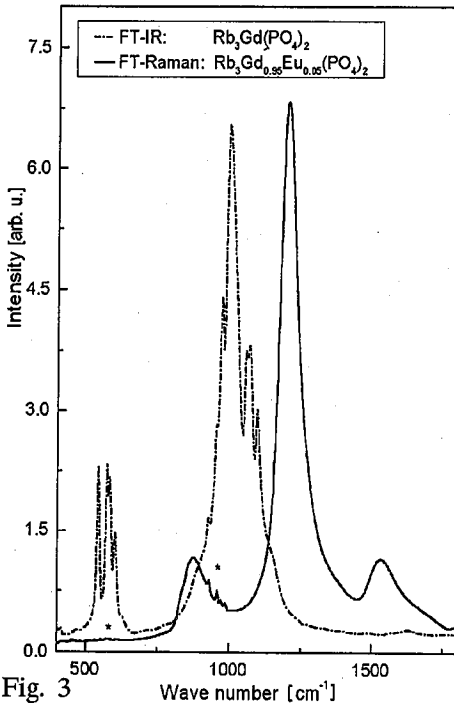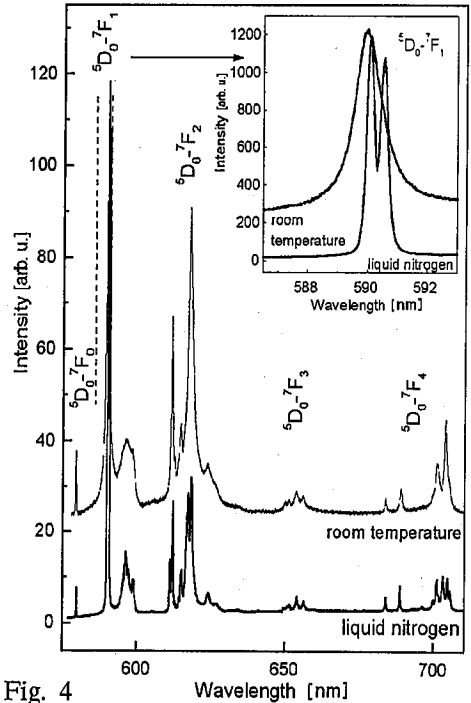

Fig. 3.   Superimposition of the FT-IR spectrum of $Rb_3Gd(PO_4)_2$ and the FT-Raman spectrum of $Rb_3Gd_{0.95}Eu_{0.05}(PO_4)_2$ with * showing the IR-active modes.

Fig. 4.   Effect of temperature on the luminescence of $K_3Eu(PO_4)_2$.

center, i.e. only one phase with one RE site, is present. The $^5D_0 \rightarrow {}^7F_0$ transition is relatively strong because allowed for the C_s, C_n, and C_{nv} point symmetries in accordance with the crystallographic information [14]. The $(2J + 1)$ degeneracy of the ^7F_J levels is completely lifted because of the low C_s point symmetry and thus the maximum number of lines was observed for most of the other $^5D_0 \rightarrow {}^7F_J$ ($J = 1-4$) transitions. Since the $^5D_0 \rightarrow {}^7F_1$ transition is more intense than the $^5D_0 \rightarrow {}^7F_2$ one the europium ion occupies a lattice site close to inversion symmetry [15]. The low intensity of the forbidden $^5D_0 \rightarrow {}^7F_3$ transition can be explained by the mixing of the $^7F_3$ wave functions with the $^7F_2$ and $^7F_4$ components. The $^5D_0 \rightarrow {}^7F_{5,6}$ transitions were not observed because of the low sensitivity of the experimental set-up which partly explains the low intensity of the $^5D_0 \rightarrow {}^7F_4$ transition as well.

Very weak luminescence was observed between 520 and 580 nm where the $^5D_1 \rightarrow {}^7F_J$ transitions should be expected. Transitions from the higher excited ^5D_J ($J = 1-4$) levels are, however, quenched efficiently by the non-radiative multiphonon deexcitation involving coupling with the high energy P–O stretching modes.
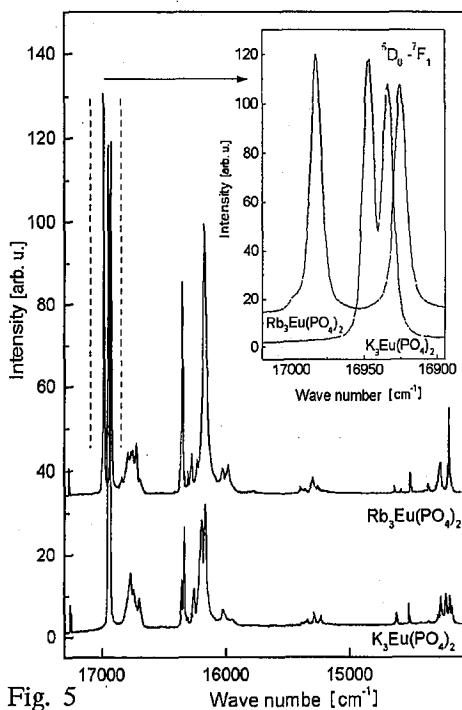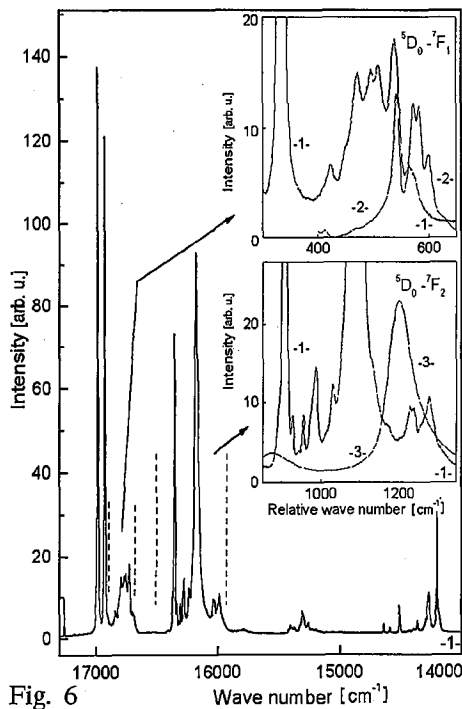

Fig. 5. Effect of the host lattice on the luminescence of $M_3Eu(PO_4)_2$ (M = K, Rb) at liquid nitrogen temperature (inset: superimposition of the luminescence of $Rb_3Eu(PO_4)_2$ and $K_3Eu(PO_4)_2$ in the region of the $^5D_0 \rightarrow {}^7F_1$ transition).

Fig. 6. Superimposition of the luminescence (-1-) by the FT-IR (-2-) of $Rb_3Eu(PO_4)_2$ (the upper inset) and FT-Raman (-3-) spectra of $Rb_3Gd(PO_4)_2$ (the lower inset) with the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of $Rb_3Eu(PO_4)_2$, respectively.

The lowering of the measuring temperature to the liquid nitrogen temperature sharpens the electronic emission lines as a result of a decrease in the homogeneous line broadening (Fig. 4). The suppression of the low energy lattice vibrations coupled to the electronic transitions leads to a better spectral resolution and allows one to separate the closely spaced electronic lines within the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$ transitions — especially for the potassium compound. The shift in the individual electronic lines in the spectra is difficult to interpret since the shrinking of the lattice on cooling on one hand increases the crystal field effect — and thus the level splitting — but, on the other hand, lowers the energies of all levels (the red shift) along with the shrinking electronic configuration. All of these effects can be seen for the $^5D_0 \rightarrow {}^7F_1$ transition (inset of Fig. 4). The intensity of vibronic side bands mostly found with the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions seems to decrease with decreasing temperature.

The general features as the splitting and intensity of the lines in the luminescence spectra of the potassium and rubidium compounds are quite similar (Fig. 5). The most pronounced difference is the larger splitting of the $^7F_1$ level for the rubidium compound (inset of Fig. 5). The bonding in the rubidium lattice is more covalent than in the potassium one which is reflected in the position of the
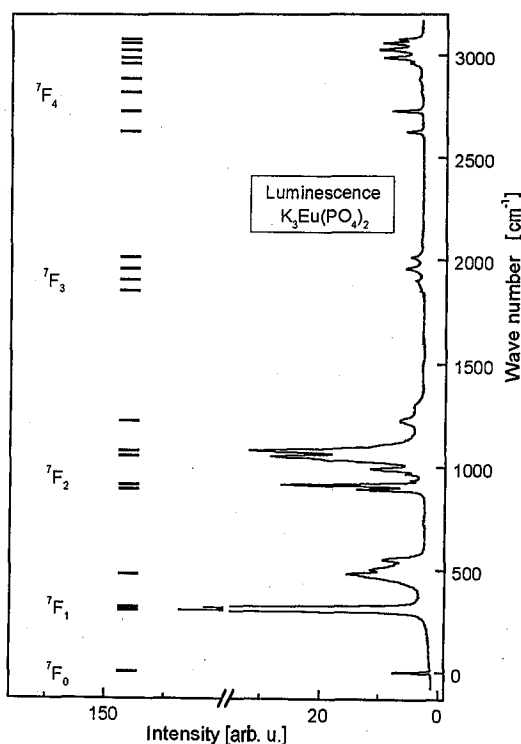

Fig. 7. Crystal field fine structure of the $^7F_{1-4}$ ground term energy level scheme of Eu^{3+} in $K_3Eu(PO_4)_2$.

$^5D_0 \rightarrow {}^7F_0$ transition (17259 and 17249 cm^{-1} for Rb$_3$Eu(PO$_4$)$_2$ and K$_3$Eu(PO$_4$)$_2$, respectively) according to the well-known nephelauxetic effect.

The superimposition of parts of the IR and luminescence spectra in the region of the $^5D_0 \rightarrow {}^7F_1$ transition illustrates the presence of the different vibronic modes in the emission spectrum of the trivalent europium (upper inset of Fig. 6). Vibronic coupling could also be identified in the range of the $^5D_0 \rightarrow {}^7F_2$ transition by superimposition of the Raman spectrum with the luminescence one (lower inset of Fig. 6).

The interpretation of the luminescence spectra explained the unexpected high number of the lines. As a result of the detailed analysis of the IR, Raman, and luminescence spectra, a preliminary $^7F_{JM}$ crystal field energy level scheme for the Eu^{3+} ion can be proposed (Fig. 7) and will be used in a subsequent analysis of the crystal field effect in the potassium and rubidium rare earth double phosphates.

Acknowledgments

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