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# Near-infrared photoluminescence in phosphate minerals and related glass–ceramics

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Fertilizing glass–ceramics were prepared and characterized by photoluminescence (PL) spectroscopy. These materials, and some of the related phosphorites, unexpectedly exhibited intense PL emission in the near-infrared region. In the 1100–1250 nm range a very intense doublet at 1161 and 1149 nm and a less intense band at 1214 nm were assigned to emission from the uncommon ionic species $Mn^{V}$. Therefore, one of the $d^2$ ions such as $Cr^{IV}$ and $Mn^{V}$ which are of growing interest in the field of solid-state lasers, was found in minerals for the first time. In order to obtain further information about these materials, structural and spectroscopic properties of the raw materials were recorded separately. As far as the coordination of $Mn^{V}$ is concerned, the hypothesis of partial substitution of $P^{V}$ by $Mn^{V}$ in the phosphate lattice appears to be quite reliable. Typical PL emission of neodymium was also observed both in glass–ceramics and in raw materials.

## 1. Introduction

In several countries there are some phosphate deposits at present unexploited because of their low economic effectiveness. On the other hand, the agrarian industry requires low-cost fertilizers that should contain useful elements for plants, such as phosphorus, potassium and micronutrients. For this purpose, the above mines can provide an interesting phosphate source, once the extracted material is mixed with potassium raw material such as feldspars and melted, so yielding glass–ceramic materials. The latter, in turn, releases the nutrient elements at a low rate, thereby avoiding any soil poisoning [1–3].

Fertilizing glass–ceramic materials were characterized by microscopic, structural and spectroscopic (in particular inductively coupled plasma (ICP) atomic emission spectrometry and photoluminescence (PL)) techniques [3].

Quite unexpectedly, samples of fertilizing glass–ceramics prepared in our laboratory exhibited intense PL emission in the near-infrared region. In the present paper we report this phenomenon and we discuss its origin and possible applicative interest.

## 2. Experimental procedure

Glass–ceramic sample A was prepared from a 1:1 mixture of powdered feldspar (from Segovia, Spain) and a phosphorite from the Logrosán mine (from Cáceres, Spain). The chemical composition of the raw materials is the following: for feldspar, 13.1 wt% $Al_2O_3$, 0.19 wt% CaO, 0.02 wt% MgO, 0.12 wt% $Fe_2O_3$, 14.4 wt%, $K_2O$, 2.31 wt% $Na_2O$, 67.3 wt% $SiO_2$ and 0.6 wt% loss on ignition (LI); for phosphorite, 1.15 wt% $Al_2O_3$, 32.0 wt% CaO, 0.19 wt% MgO, 0.22 wt% $Fe_2O_3$, 0.07 wt% $K_2O$, 0.33 wt% $Na_2O$, 23.1 wt% $P_2O_5$, 31.0 wt% $SiO_2$, 0.02 wt% MnO and 9.82 wt% LI.

The mixture was heated in an aluminosilicate crucible with a constant temperature gradient of 10 °C $min^{-1}$ until the temperature reached 1300 °C and kept at this temperature for 30 min. The melt was subsequently poured into distilled water at room temperature. The obtained material was milled down to a grain size of less than 1 mm in a tungsten carbide mortar.

The chemical analysis was performed with a sequential spectrometer (Jobin Yvon 38-VHR) with an ICP source and equipped with a high-resolution monochromator (3600 grooves $mm^{-1}$) and an auxiliary monochromator (1200 grooves $mm^{-1}$), making use of an internal standard.

The PL spectra was recorded by means of a custom-made apparatus (Laser Point), equipped with a 25 mW He–Ne laser (NEC), a grating spectrometer (Jobin Yvon 640-HR) with a reciprocal dispersion of 2.4 nm $mm^{-1}$, a liquid-$N_2$-cooled germanium detector (North Coast EO817L) and a helium-flux cryostat (TBT-Alphagaz) [4]. The homogeneity of all investigated samples was checked by measuring the PL spectra of several grains.

## 3. Results and discussion

The PL spectrum of sample A recorded at room temperature (Fig. 1) exhibits in the 1100–1250 nm region a very intense doublet at 1161 and 1149 nm (8613 and 8696 $cm^{-1}$, respectively), and a less intense broad band at 1214 nm (8237 $cm^{-1}$).

On the basis of the literature [5, 6], in particular concerning the energy level scheme [6] we assigned the above doublet and band to emission from $Mn^{V}$ ions.

There are few papers in literature reporting the occurrence and spectroscopic properties of such uncommon ionic species [5, 7–10], in spite of the growing interest in the field of solid-state lasers [11] and of fibre-optics communications [12] of the $d^2$ ions, especially $Cr^{IV}$ and $Mn^{V}$.

The less intense band peak at about 1060 nm cannot be related to $Mn^{V}$ and, owing to its shape and position, it was ascribed to the luminescence of $Nd^{III}$ [13–15]. The spectrum of a neodymium sample B glass is reported in Fig. 1 for comparison. The spectrum of sample A shows, even though less intense, the same spectral features as sample B in the 850–900 and 1300–1350 nm regions.

Finally, the narrow line at about 1265 nm is an instrumental artefact related to the He–Ne laser light.

The structural and spectroscopic properties of the raw materials were recorded separately. While no $Mn^{V}$ or $Nd^{III}$ photoemission was shown by the feldspar, the PL spectrum (Fig. 2) of the Logrosan phosphorite (sample C) recorded at room temperature shows the same main features as sample A in the 1100–1250 nm region (Fig. 1).

This behaviour, related to the presence of $Mn^{V}$ is common to other phosphorites; see for instance the PL (Fig. 2) spectrum of the Zarza la Mayor

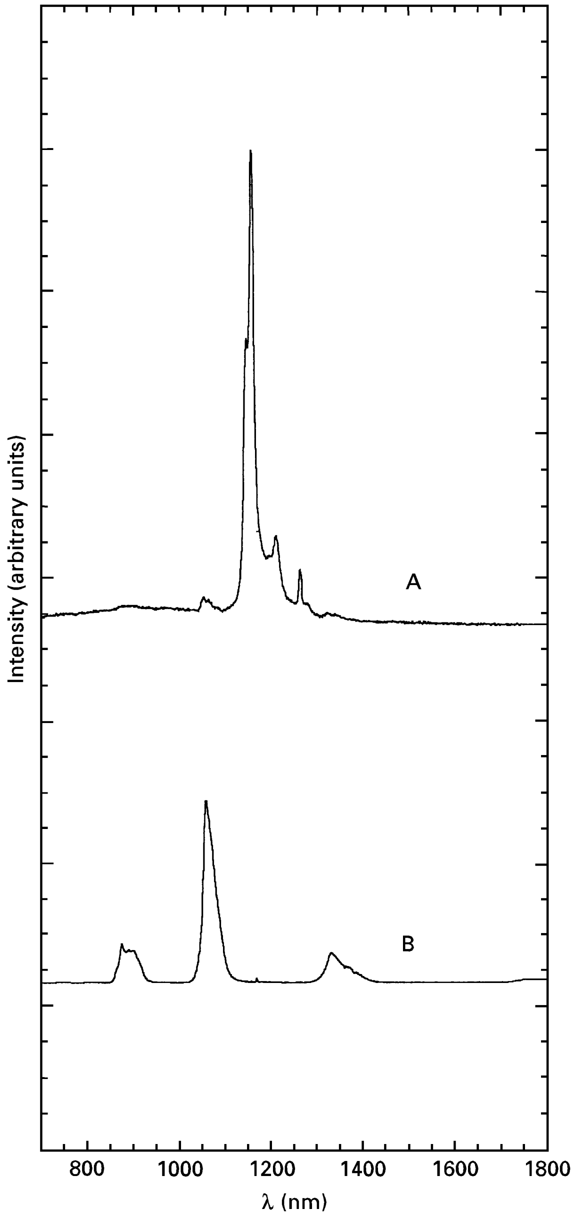

*Figure 1* PL spectra at room temperature of the glass–ceramic material sample A and of a neodymium-doped glass sample B.

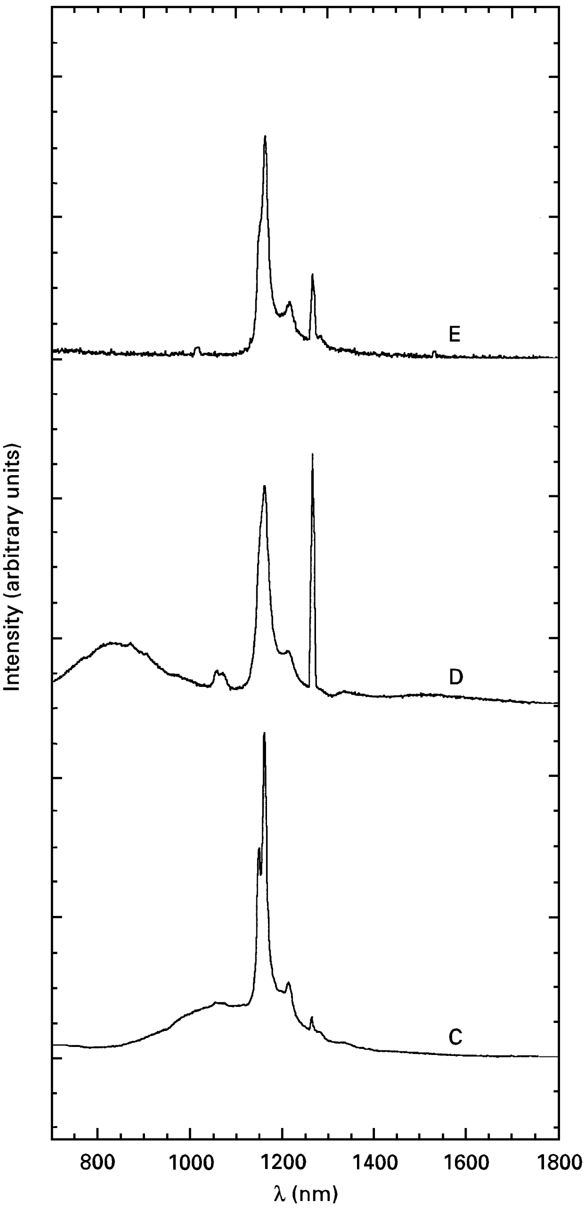

*Figure 2* PL spectra at room temperature of the phosphorite samples C and D and of the triplite sample E.

phosphorite (sample D) also coming from Cáceres (Spain). This spectrum exhibits evidence of $Nd^{III}$ impurities. This cannot be observed for the Logrosan sample because of the presence of an additional unassigned broad band in the same spectral region.

The X-ray diffraction (XRD) powder spectrum [3] of the phosphorite indicates that this material is mostly crystalline, the main phases being hydroxyapatite and/or fluoroapatite (we are not able to distinguish between the two by this technique) [16].

As far as the coordination of $Mn^V$ is concerned, the hypothesis of partial substitution of $P^V$ by $Mn^V$ in the phosphate lattice [5] appears to be quite reliable. Therefore the Mn impurity should occupy the same cystalline site. Moreover, the full width at half-maximum of the most intense peak (27 nm) is consistent with a crystalline environment.

We examine here (Fig. 2) also the PL spectrum of the mineral triplite sample E, which is a manganese and iron phosphate [17, 18]. Comparison of the latter spectrum with that of sample A not only gives support to our assignments as far as $Mn^V$ is concerned but also confirms the hypothesis of partial substitution of $P^V$ by $Mn^V$ in the phosphate lattice.

The emission line peaked at 1214 nm, well evident in the spectra of samples A, C, D and E is a vibrational side band and it is probably due to $Mn^V$ in a different site in the lattice.

On the basis of the above considerations, we are dealing with a $d^2$ first-row transition-metal ion surrounded by four oxygen atoms in an approximately tetrahedral configuration. From a spectroscopic point of view the system can be undoubtedly treated by the simple model of the crystal-field theory, through which we are able to predict the number of electronic multiplets into which the states are split, and their order and symmetry.

The first excited state of $Mn^V$ in the $T_d$ symmetry is $^1E(et_2)$ (partially mixed with the higher $^3T_2(et_2)$ state), which relaxes radiatively onto the ground state $^3A_2(e^2)$. The emitting state appears to be split into its two components ($E_s = E_{d_{z^2}}$ and $E_a = E_{d_{x^2-y^2}}$); the corresponding bands are at 1149 nm (8703 $cm^{-1}$) and 1161 nm (8613 $cm^{-1}$) with $\Delta E = 83\ cm^{-1}$, which is small when compared with other crystals (see [8]).

This behaviour is probably due to a weak $C_{3v}$ distortion with respect to the tetrahedral symmetry in the environment of the luminescent ion. This distortion would result in a variation in the mean distance between the central Mn and one of the immediately surrounding oxygen atoms, so that this Mn–O axis becomes the unique symmetry axis ($C_3$) of the arrangement. The distortion extent seems to be smaller for the substituting $Mn^V$ ion than for the structural $P^V$ ion; this could be an explanation for the occurrence of $Mn^V$ in several mineral phosphates (see below for triplite), while the oxidation state V is unusual for Mn in aqueous solution.

The above interpretation of the PL spectra is supported by the temperature dependence of the relative spectral intensities of the two bands at 1149 and 1161 nm (Fig. 3). In fact, according to Boltzmann equilibrium between the two components, the thermal population of the higher-energy component of the doublet (at 1149 nm) decreases upon cooling.

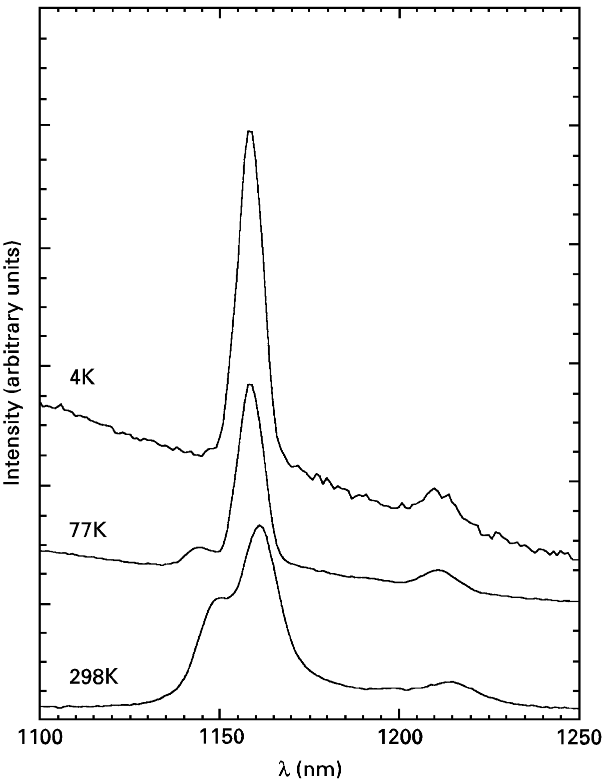

*Figure 3* PL spectra of the glass–ceramic material A at 298, 77 and 4 K.

## 4. Conclusions

For the first time, at least to our knowledge, one of the $d^2$ ions such as $Cr^{IV}$ and $Mn^V$ was found in raw mineral materials. In fact, $Mn^V$ appears to be unexpectedly common in the solid state, and particularly in phosphate-related crystals.

Moreover, it is noteworthy that, in spite of the above violent mechanical and thermal treatment, the luminescent properties are substantially maintained.

The above considerations further encourages the investigation, at present in progress, of the chemical behaviour and physical properties of manganese in the title materials and related compounds [19].

The ability of PL to demonstrate small differences within a given class of compounds, often deriving from impurities in very low concentration, and to relate them to the origin of the minerals, has been discussed elsewhere [20, 21].

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