

Evidence of Coordinate Field Index Influence on Upconversion Properties in Er³⁺ Doped Tellurite Glasses

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Abstract Tellurite glasses doped the same concentration of Er³⁺ were prepared by conventional melting procedure, and their upconversion luminescences were measured. Two green emission bands at 521 nm and 550 nm and one red emission band at 657 nm were observed. This paper reported on the deduction of coordinate field index, which was proposed by deducing from Pauling's rules on the basis of Zachariasen's random network theory, it was defined to the qualitative index that stand for the deviation of a given truly coordinate polyhedron from the hypothetical one. It can be used to rationalize the remarkable and regularity variation in the upconversion intensity in our prepared tellurite glasses.

Keywords Coordinate field index · Pauling's rules · Zachariasen's random network theory · Upconversion · Tellurite glasses

Introduction

Upconversion fiber laser is one of the three methods of making the short-wavelength compact lasers. Due to their potential application in fields [1–4] of information process, data storage, display technology, undersea transmission, and medicine, so in the new millennium, extensive research has been paid to upconversion of rare-earth doped materials. Particularly, tellurite glasses have been extensively investigated because of their relative low phonon energy, high refractive index, good corrosion resistance, and high thermal stability [2].

It is well known that Pauling's rules [5] have been widely used to predict and rationalize the ionic structure [6–7]. As to materials science and engineering, based on Zachariasen's random network theory, the glasses forming theory, many researchers used Pauling's rules to predict the ability of glasses formation [8].

In this article, tellurite glasses (MKT: TeO₂–MgO–K₂O) doped the same concentration of Er³⁺ were prepared by conventional melting procedure, and their upconversion spectra were measured, the glasses compositions (in mol%) are shown in Table 1. In our research, coordinate field index, which can be deduced from Pauling's rules and bond valence theory, can be used to predict the intact of glasses' structure, and then we can rationalize the remarkable and regulative variation in intensity of upconversion luminescence of the glasses.

Pauling's rules and coordinate field index

Linus Pauling, one of the world's greatest scientists and peace activists, is the only person to date to have won two unshared Noble prizes, the first one was awarded for his landmark research on the nature of the chemical bond and its application to understanding the structure of complex substances, the second acknowledged his courageous protest against atmospheric nuclear testing and his championship of international peace.

Pauling's rules, a series of structural principles for ionic crystals, mainly include the following five rules:

- (1) Pauling's rule one: Coordination polyhedron
A coordination polyhedron of anions is formed around every cation (and vice-versa); it will only be stable if the cation is in contact with each of its neighbors.

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Table 1 The compositions of tellurite glasses.

Sample No	Composition (in mol%)			
	TeO ₂	MgO	K ₂ O	Er ₂ O ₃
MKT1	80	9.5	10	0.5
MKT2	70	19.5	10	0.5
MKT3	70	9.5	20	0.5
MKT4	60	29.5	10	0.5
MKT5	60	19.5	20	0.5

(2) Pauling's rule two: Bond strength (Electrostatic valence) principle

In a stable ionic structure, the charge on an ion is balanced by the sum of electrostatic bond strengths to the ions in its coordination polyhedron, that is to say, a stable ionic structure must be arranged to preserve local electroneutrality.

(3) Pauling's rule three: Polyhedral linking

The stability of structure with different types of polyhedral linking is: Vertex-sharing > edge-sharing > face-sharing. Effect is largest for cation with high charge and low coordination number.

(4) Pauling's rule four: Cation evasion in > binaries

In a crystal containing different cations, those of high valence and small coordination number tend not to share polyhedron elements with each other.

(5) Pauling's rule five: Environmental homogeneity

The numbers of essentially different kinds of constituents in a crystal tend to be small as far as possible, i.e., similar environments for chemically similar atoms.

The term "glass" is commonly used to mean the fusion product of inorganic materials which have been cooled to a rigid condition without crystallizing. The well known and classical theory of glasses forming was proposed in 1932 by Zachariasen. Zachariasen's random network theory [9–10], the rules for the forming of low-order 3-dimensional network, assumed that oxygen polyhedrons found in oxide crystals (triangular, tetrahedral and octahedral) would also occur in glasses, the only difference being the relative orientation of polyhedron should be variable in glasses, giving rise to a nonperiodic structure.

The theory assumes that the following rules are valid for the formation of glasses:

- (1) An oxygen atom is linked to no more than two glass forming atoms.
- (2) The coordination number of glass formed is small, that is to say, an oxide of compound tends to form a glass, if it easily forms polyhedron groups as smallest building units.
- (3) Anions (e.g. O²⁻, S²⁻, and F⁻) should not build more than two central atoms of a polyhedron. Thus, the anion

polyhedron share corners with each other, but not edges or faces.

- (4) At least three corners of a polyhedron must connect with neighbor polyhedrons.

In comparison with Pauling's rule, the random network theory bases itself on coordination polyhedrons. More useful things were expected to deduct from Pauling's rules.

According to Pauling's rules two (bond strength), for a cation M^{m+} surrounded by an anion X^{x-}, the electrostatic bond strength (abbreviate as: *S*) of the cation is defined as:

$$S = \frac{Z(+)}{n(+)} \quad (1)$$

Where *Z* (+) is the charge of the cations (M^{m+}), *n* (+) mean the coordination number of the cation.

Similarly, the electrostatic bond strength of the anion is also written as:

$$S = \frac{Z(-)}{n(-)} \quad (2)$$

As to electroneutrality, for each anion (cation), the sum of the electrostatic bond strength for the surrounding cations (anions) must balance the negative (positive) charge on the anion (cation).

$$\sum \frac{Z(+)}{n(+)} = x \quad (3)$$

$$\sum \frac{Z(-)}{n(-)} = m \quad (4)$$

From Eqs. (1)–(4), the following Equation can be easily deduced:

$$\frac{Z(+)}{n(+)} = \frac{Z(-)}{n(-)} \quad (5)$$

According to Pauling's rule one, coordination number is determined by the ratio of ionic radii, γ^+/γ^- with values derived from the geometric contact criterion. Thus, *n* is the function of radii

$$n = f(\gamma, \gamma^+, \gamma^-) \quad (6)$$

where γ means the coordinate radius of polyhedron, γ^+ is the radius of the cation and γ^- the radius of the anion.

Then, Eq. (5) can be rewritten as:

$$\sum \frac{Z(+)}{f(\gamma, \gamma^+, \gamma^-)} = \sum \frac{Z(-)}{f(\gamma, \gamma^-, \gamma^+)} \quad (7)$$

Therefore, we can define FI as:

$$FI = \sum \frac{Z(+)/\gamma^+}{Z(-)/\gamma^-} \tag{8}$$

$$\Delta FI = FI - FI^* \tag{9}$$

where FI, a qualitative index represent the intact of the truly coordination polyhedron, FI* is the corresponding qualitative index of the hypothetical polyhedron of the network-former, ΔFI is defined as the coordinate field index and stands for the intact of a truly coordination polyhedron, i.e., the deviation of a given truly coordinate polyhedron from the hypothetical one. The deviation will become more serious with increasing ΔFI, meaning that the intact of a truly given polyhedron may be worse.

Experiment

The starting materials for the Er³⁺ doped MKT glasses were all analytical g chemicals of TeO₂, K₂CO₃, MgCO₃ and Er₂O₃. According to the composition given in Table 1, the well mixed powder were melted at 850 for 30 min using an electric furnace, the glasses melts was poured into a stainless steal mould and annealed in a muffle oven at their T_g points. The annealed glasses were cut into 15 mm × 15 mm × 1.5 mm pieces and carefully polished for optical measurements.

Upconversion luminescence measurements were performed by a system of 980 or 800 nm LD pumping and a Triax-320 spectrophotometer detecting. The infrared spectra were obtained using Bruker VECTOE-33 infrared spectrometer.

All the measurements were done at room temperature.

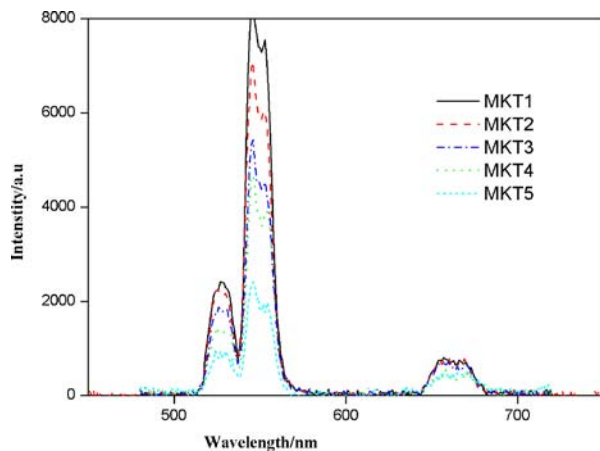


Fig. 1 The upconversion spectra of Er³⁺ doped

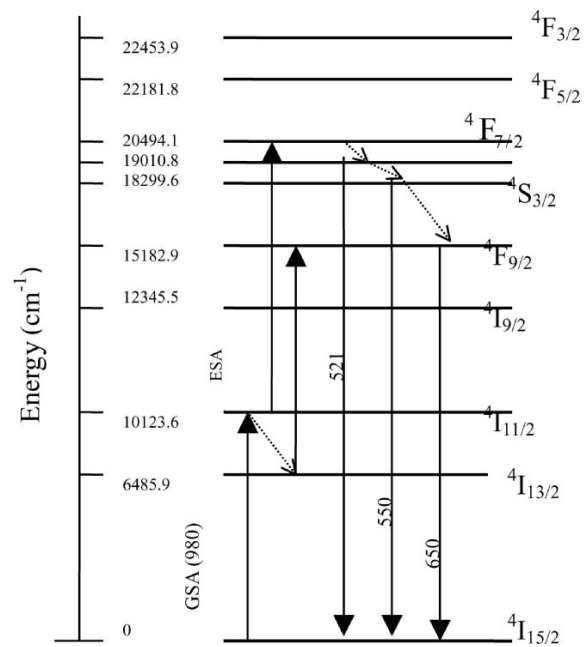


Fig. 2 The simple energy level diagram of Er³⁺ in TMK glasses

Results and discussion

The room temperature upconversion emission spectra excited with 980 nm LD lasers are presented in Fig. 1. Two green emission bands at 521 and 550 nm, corresponding to the transitions of ²H_{11/2}→⁴I_{15/2} and ⁴S_{3/2}→⁴I_{15/2}, according to the simple energy level diagram of Er³⁺ showing in Fig. 2, they are respectively, one red emission band at 650 nm, due to transition of ⁴F_{9/2}→⁴I_{15/2}, were observed. The tree peak intensity of upconversion luminescence obviously increased in the sequence of MKT1, MKT2, MKT3, MKT4, and MKT5.

As shown in Table 1 the concentration of Er³⁺ are 0.5 mol% for all the five samples, so the concentration and the mechanism are not the reason for the remarkable variation in the intensity of upconversion luminescence.

It is well known that the phonon energy is a key index to determine the upconversion luminescence, so Infrared spectra were measured. However, as showing in Fig. 3, the differentiation of phonon energy being so small, it is impossible to detect so remarkable difference. The upconversion mechanism and corresponding processes can be obtained from the relationship between the intensity of blue luminescence and the excitation power. Fig. 3 shows us the intensity of 546 nm green luminescence as a function of the excitation power, the plots are in log (I_{up}) versus log (I_{IR}) [11], referring to Fig. 2, these results suggested that the ²H_{11/2} level is populated through a two-photon step process. According to Fig. 2, we believed that the mechanism is mainly excited by the excited state absorption (ESA) process, an Er³⁺ ion was

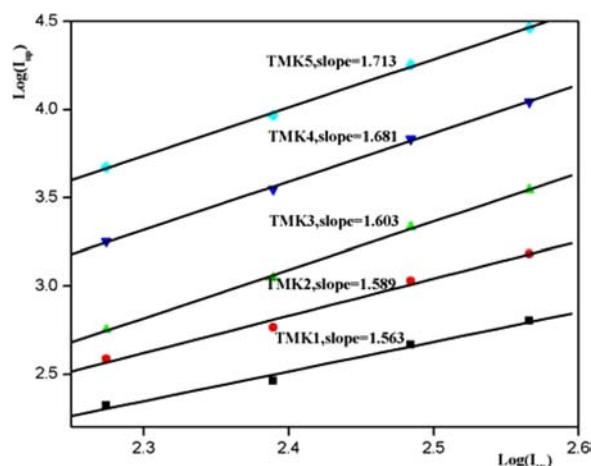


Fig. 3 The 546nm upconversion luminescence intensity VS pumping power. They are shown in double-log () function

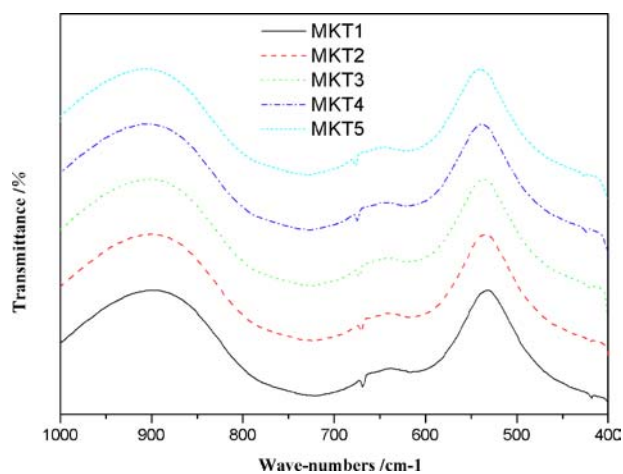


Fig. 4 The Infrared spectra of Er³⁺ doped MKT

excited from ground state $^4I_{15/2}$ to the excited state $^4I_{11/2}$, and the ions in level non-radiatively relax to $^4I_{13/2}$. Because of the energy match, so the excited Er³⁺ ions in $^4I_{11/2}$ and $^4I_{13/2}$ level can absorb another incident photon of 980nm LD, and then rose to $^4F_{7/2}$ level and $^4F_{9/2}$ level, respectively. The ions in $^4F_{7/2}$ level relax to the $^2H_{11/2}$ via non-radiatively transition. Similarly, those ions in $^2H_{11/2}$ level may also non-radiatively relax to $^4S_{3/2}$ level, and then $^4S_{3/2}$ level relax to $4F_{9/2}$ level. When the ions in $^2H_{11/2}$ level radiatively relax to the ground level $^4I_{15/2}$, it emitted to 523nm green luminescence; similarly, the ions in level $^4S_{3/2}$, $^4F_{9/2}$ radiatively relax to the ground level $^4I_{15/2}$, they respectively emitted the 546nm and 657nm upconversion luminescence. So the upconversion mechanism is also not accounted for the remarkable and regular variation in upconversion luminescence intensity.

It is well known that the phonon energy is a key index to determinate the upconversion luminescence, so Infrared spectra were measured. However, as showing in Fig. 4, the

Table 2 The coordinate field index of MKT glasses.

Sample	FI	Δ FI
MKT1	3.6414	0.6009
MKT2	3.4058	0.8365
MKT3	3.2683	0.9740
MKT4	3.1819	1.0604
MKT5	3.0385	1.2038

Note: 1. FI* = 4.2423; 2. For the original data (Z , n , γ^+ , and γ^-) for calculation we can refer to: Peiwen Lu, The Basic of Inorganic Materials Science, Wuhan University of Technology Press, Wuhan, People's Republic of China, 1996, Appendix 3.

differentiation of phonon energy is so small, it is impossible to induct so remarkable differentiae.

In order to rationalize the remarkable variation in the intensity of upconversion luminescence, the coordinate field index were calculated according to Eq. (9). As we can find in Table 2, Δ FI increase in the sequence of MKT n ($n = 1, 2, 3, 4$ and 5, respectively), thus indicating that the deviation become more serious with increasing n . It is well known that K₂O and MgO are all the network-modifiers, so the destruction of glasses network will become worse with increase in the concentration of K₂O and MgO, then the defect will become more obvious, thus absorption and scattering of the light will be worse, therefore, the upconversion intensity are weaker.

Conclusions

The upconversion spectra of MKT glasses were measured. Coordinate field index (Δ FI) was deduced from Pauling's rules on the basis of Zachariasen's random network theory. To our best knowledge, Δ FI, which was first proposed, can be used to predict the intact of glasses network, the larger the number of Δ FI, the more serious the defect of the network. Application of it can rationalize the remarkable difference in the intensity of samples' upconversion luminescence. With increasing coordinate field index Δ FI, the defects become worse in the sequence of MKT1, MKT2, MKT3, MKT4, and MKT5.

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